GAS PHASE OXIDATION OF HYDROCARBONS

Thesis

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Doctor of Philosophy

by

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ABSTRACT OF THESIS

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Title of Thesis GAS PHASE OXIDATION OF HYDROCARBONS.

The slow oxidation of isobutane in the temperature range 270 - 330°C has been investigated, using katharometer detection for product analyses, over an eighteen fold change in hydrocarbon/oxygen ratio. Variation of temperature and hydrocarbon/oxygen ratio had little effect on the relative yields of products. Under all conditions studied, 70 - 80% of the isobutane initially consumed was converted to isobutene. Minor oxygenated products were(in order of decreasing abundance) acetone, propylene, carbon dioxide, isobutene oxide, propionaldehyde, acetaldehyde, carbon monoxide, methanol, propylene oxide, ethylene, methacrolein, and methane.

Oxidation of the main primary product, isobutene, was shown to occur in the middle stages of isobutane oxidation. Isobutane oxidations at low conversions (1 - 2%) of isobutane have been carried out using flame ionisation detection for product analyses. Under these conditions, only primary products were observed. Hydrocarbon/oxygen ratio and reaction temperature were again varied over a wide range. 80% of the isobutane consumed was converted to isobutene. Minor product distribution was almost independent of oxygen pressure. The effects of variation of temperature and mixture composition on minor product distribution were such that product formation could not be explained by isomerisation and decomposition reactions of butyl peroxy radicals.

Studies of competitive oxidations of isobutane/propane mixtures at 300°C have shown that the radical attacking hydrocarbons in the early stages of alkane oxidations is HO_2. The formation of the olefin of the same carbon number as the parent alkane results from an HO_2 radical chain.

Investigation of the initial stages of propane oxidation at 300°C has shown that 78% of the propane consumed is converted to propylene. Minor oxygenated products detected were acetaldehyde, propylene oxide, propionaldehyde, acetone, methanol and ethanol. The formation of these minor products has been qualitatively explained on the basis of isomerisation and decomposition reactions of iso-

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and n- propyl peroxy radicals.

Isobutane oxidations at 330°C under identical experimental conditions gave irreproducible results which could be explained only by a variation in the nature of the reaction vessel surface. Isobutane oxidations have been carried out in reaction vessels of widely varying surfaces and product distributions compared to those obtained in clean Pyrex vessels under similar conditions. Although the ratio of isobutene to minor products did not vary greatly, the distribution of the minor product yields was drastically altered by changing from acidic to salt coated reaction vessel surfaces. These results suggested that minor product formation occurred mainly by heterogeneous processes and a scheme has been proposed to account for this in isobutane oxidation.

$$i\ C_4H_{10} + HO_2 = C_4H_9 + H_2O_2$$

$$C_4H_9 + O_2 = C_4H_8 + HO_2$$

$$C_4H_9 + O_2 = C_4H_9O_2$$

$$C_4H_9O_2 \xrightarrow{wall} \text{complex mixture of minor products.}$$

Wall processes have been shown to be of importance in the formation of minor oxygenated products in isobutane oxidation at 300°C.

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ABBREVIATIONS

The following abbreviations have been used throughout the text and tables.

P.A.	=	Propionaldehyde
I.B.A.	=	Isobutyraldehyde
M.A.	=	Methacrolein
ΔP	=	Pressure rise during oxidation
τ	=	length of induction period
ϕ	=	acceleration constant
ρ_{max}	=	maximum rate of reaction
B.A.	=	Boric Acid coated reaction vessel
H.F.	=	Reaction vessel washed with hydrofluoric acid
C.P.	=	Clean Pyrex reaction vessel

Sample No. X/Y indicates that the analysis is for the Yth sample from Run X.

Pressures throughout are given in mm Hg.

Initial Fractional Product yields are given in terms of carbon content i.e. in mm atoms C per product/mm atoms C in total product.

Introduction

1. Slow oxidation of hydrocarbons.

1.1 Early Theories.

Until 1860, the accepted theory of hydrocarbon oxidation was that of Preferential Combustion of Hydrogen, this theory being based on the observation that a flame deposited carbon when oxygen weak mixtures were combusted. This theory became untenable when Kersten [1] identified hydrogen in the interconal gases of the combustion of hydrocarbons.

A more detailed investigation of the phenomenon of combustion was carried out by Bone and co-workers [2] in the years 1900-1912. The most important results of these new experiments were the discoveries of intermediate compounds, such as aldehydes and acids, in hydrocarbons undergoing slow oxidation. These discoveries led Bone to suggest that the oxidation proceeded by a stepwise degradation of the molecules rather than by the complete destruction of each molecule in turn. Bone elaborated a suggestion put forward by Armstrong [3] in 1874 that a hydrocarbon undergoing oxidation was degraded by a series of hydroxylations and enlarged this idea into a comprehensive theory of combustion. All the intermediates in the oxidation could be explained by the replacement of successive C-H bonds by C-OH bonds, e.g. for ethane,

$$CH_3\ CH_3 \longrightarrow CH_3CH_2OH \longrightarrow CH_3CH(OH)_2 \longrightarrow CH_3CHO + H_2O$$
$$\longrightarrow CH_3COOH \rightarrow CH_2(OH)COOH \longrightarrow CH_2O + H_2O + CO$$
$$\longrightarrow HCOOH \rightarrow H_2O + CO \qquad\qquad \downarrow$$
$$H_2 + CO$$

Although this theory could explain the formation of aldehydes and acids, a great weakness lay in the failure to detect the principal intermediate, the

alcohol. This defect was partially remedied by Newitt and Haffner [4] who observed that methanol was formed in the high pressure oxidation of methane. In a re-investigation of the oxidation of methane, Bone [5] invalidated his own theory by showing that the stationary state concentration of formaldehyde was greater than that of methanol whereas, since methanol oxidises more slowly than formaldehyde, methanol should have a greater stationary concentration than formaldehyde.

For the last ten years of its life, the hydroxylation theory was rivalled by several other theories which were, in the main, the result of the development of the ideas of chain reactions. Before going on to deal with more recent theories of combustion, it is convenient to give an account of the development of the theory of chain reactions which forms the basis of modern views of hydrocarbon oxidation.

1.2. The Development of Chain Theories.

The idea of a chain reaction was first put forward in 1913 by Bodenstein [6] to account for the high quantum yield of the photochemical reaction of hydrogen with chlorine. Bodenstein suggested chains involving electrons but this idea was later modified by Nernst [7] who suggested an atomic chain. In 1923, Christiansen and Kramers [8] introduced energy chain reactions to account for the abnormally high speeds of some first order reactions. They supposed that thermally excited molecules could pass on their energy to molecules of reaction products which could in turn, by collision with reactant molecules, bring about their decomposition into energy rich products. In a subsequent paper, Christiansen[9] showed that the phenomenon of negative catalysis could be explained if it were supposed that the negative catalyst acted as a chain breaker.

Almost immediately, the Chain Theory was successfully applied to other similar reactions, such as the oxidation of aldehydes [10], the gas phase

oxidation of hydrocarbons [11] and the hydrogen-oxygen reaction [12].

Since the suggestion of Bonhoeffer and Haber [13] in 1931 that a radical chain operated in the hydrogen-oxygen reaction and the advancement by Backstrom [14] in 1934 of a radical mechanism for aldehyde oxidation, thermal chains have been discarded and nearly all modern chain reaction schemes involve free radicals.

A critical analysis and survey of chain theory was carried out by Semenov [15] who had contributed extensively to the theory and the results of his survey were published in his book "Chemical Kinetics and Chain Reactions". From the point of view of hydrocarbon oxidations, one of the most important of Semenov's ideas was the degenerate or delayed branching chain. In a branching chain, each carrier reacts and produces more than one new carrier. This continually increasing number of chain carriers leads to an acceleration in the reaction rate. Chain carriers may react in three general ways, 1) to produce one chain carrier thus propagating the primary chain, 2) to produce more than one new carrier thus causing branching to occur, and 3) to give no new chain carrier thus effectively breaking the link.

Now, if δ is the probability of branching at any link,

β is the probability of chain breaking at any link,

n_0 is the number of initial chain carriers,

$\omega(t)$ is the velocity of the reaction,

and $\Delta\tau$ is the time for which an active centre exists before entering the reaction,

Semenov deduced that the velocity of the reaction at any time, t, was given by

$$\omega(t) = A(e^{\phi t} - 1)$$

which, for large values of t reduced to $\omega(t) = Ae^{\phi t}$ where

$$A = n_0/(\delta-\beta) \text{ and } \phi = (\delta-\beta)/\Delta\tau$$

In the case of the oxidation of organic compounds, the rate of reaction in the early stages increases slowly and exponentially with time. The rate of acceleration of the reaction, is, however, too small to be explained by the above theory of simple branching. In order to explain observed values in hydrocarbon and other oxidations, Semenov had to conclude that $\Delta\tau$ had to be of the order of minutes or hours. He suggested that, in such cases, a moderately stable intermediate, with an average life greater than that of the primary chains, was formed which reacted slowly to produce a supply of new radicals. If the development of the chains were sufficiently slow, the rates of reaction would always remain finite since the increasing consumption of reactants would eventually cause a fall in the rate before the system became thermally unstable.

In a gas phase reaction, where the amount reacted after time t, x, is proportional to the pressure change ΔP, integration of the equation

$$\omega(t) = \frac{dx}{dt} = k\frac{d(\Delta P)}{dt} = Ae^{\phi t}$$

leads to $\Delta P = k^{-1}A\phi^{-1}e^{\phi t}$ i.e. $\Delta P = Ne^{\phi t}$

Therefore, in gas phase oxidations which are also degenerate branching reactions, plotting either $\log \Delta P$ against t or $d\Delta P/dt$ against ΔP should give a straight line of gradient ϕ.

1.3. General Features of Oxidation Systems

Oxidations of hydrocarbons are generally carried out at temperatures between 250°C and 600°C and at pressures less than atmospheric. Catalysed oxidations, however, may occur at temperatures about 100°C lower than those at which uncatalysed oxidations take place. The minimum temperatures at which oxidation occurs decreases as the length of the hydrocarbon chain increases. Branched chain hydrocarbons undergo oxidation more slowly than the corresponding straight chain compounds. Hydrocarbon oxidations are characterised by an induction period, an initial period

of time which may be of the order of minutes or hours during which little reaction occurs. This induction period, τ, generally decreases with increase in reaction temperature and increase in reaction mixture pressure. After the induction period, a gradual acceleration in the rate of pressure rise takes place until the maximum rate of reaction, P_{MAX}, is reached. At this point, the rate of pressure rise falls off sharply in fuel rich mixtures and slowly in oxygen rich mixtures. The formation of water and carbon monoxide is largely responsible for the pressure rise observed during an oxidation of a hydrocarbon. Hydrocarbon oxidations are generally autocatalytic as a reaction product may accelerate the rate of reaction as a result of its oxidation or decomposition to yield more free radicals. The characteristics of degenerate branching reactions are usually observed, i.e. plots of $d\Delta P/dt$ against ΔP give straight lines of gradient ϕ, ϕ being the acceleration constant. The pressure rise in the reaction vessel increases exponentially with time according to the equation $\Delta P = Ae^{\phi t}$ where A is a constant.

The occurrence of cool flames is one of the characteristic features of the low temperature oxidation ($<400^{\circ}C$). During a cool flame, the reaction proceeds at a greatly enhanced rate due to instability of the reaction system and a pale blue light is emitted from the reaction vessel. The emission of light is accompanied by a sudden rise and fall of pressure in the reaction vessel. At higher critical pressures, the reaction following the cool flame results in a blue flame followed by ignition. This phenomenon is known as two-stage ignition. As many as five cool flames may be observed for a hydrocarbon-oxygen system before true ignition takes place. Although the pressures at which cool flames are formed are different for different hydrocarbon-oxygen systems, the temperature limits are of the same order for all systems. The lower limit of cool flame production lies between $220^{\circ}C$ and $270^{\circ}C$ and the upper limit between $350^{\circ}C$ and $400^{\circ}C$.

Another feature of hydrocarbon oxidations is the "negative temperature coefficient". Although rates of reaction may follow the Arrhenius equation over small temperature ranges, studies of variations of maximum rates with temperatures have shown that a plot of maximum rate against temperature has a maximum followed by a minimum as temperature increases. Below 350°, the maximum rate increases with temperature but in the region 350°C - 400°C the rate decreases with temperature thus giving a maximum in the plot and a negative temperature coefficient. At higher temperatures, the maximum rate again increases with temperature and the plot thus shows a minimum. The region below 350°C - 400°C is referred to as the "low temperature region" and that above this range as the "high temperature region".

In "low temperature" oxidations, typical products are aldehydes, ketones, alcohols, acids and hydroperoxides. Hydrogen peroxide, hydrogen, methane and olefins become important at high temperatures. This difference in product distribution has led to the accepted idea that different mechanisms operate in oxidations in the two temperature regions.

1.4 Recent Theories of Hydrocarbon Oxidation.

At the same time as the limitations of the hydroxylation theory became evident, Norrish [16] proposed at atom chain theory for the oxidation of methane, ethane and ethylene. As shown below, methane oxidation was considered to be an alternative formation of free methylene radicals and oxygen atoms with the steady generation of formaldehyde.

i.e. Propagation $O + CH_4 = CH_2 + H_2O$

$CH_2 + O_2 = CH_2O + O$

Branching $CH_2O + O_2 = HCOOH + O$

Termination $O + CH_4 + X = CH_3OH + X$

$O + \text{wall} = \frac{1}{2}O_2$

Whereas Bone [2] visualised the aldehyde as being produced from the alcohol,

Norrish proposed that the aldehyde was formed as a direct result of the chain mechanism.

Ubbelohde [17], who objected to Norrish's theory on the grounds that the formation of oxygen atoms was unlikely because of steric factors, proposed a chain mechanism producing peroxides. The radical RCO_3, which Backstrom had surmised played a part in liquid phase aldehyde oxidations, was proposed as the initiator in hydrocarbon oxidation as shown in the following scheme:

Initiation	$RCO_3 + RCH_3 = R\dot{C}(O-OH) = O + RCH_2$
Propagation	$RCH_2 + O_2 = RCH_2OO$
	$RCH_2OO + RCH_3 = RCH_2OOH + RCH_2$
Branching	$RCH_2OOH = RCH_2O + OH$

Although this scheme was similar to that proposed by Norrish, in that the propagating steps involved a chain reaction, it was considered that a hydroperoxide rather than an aldehyde was produced.

The general concept of these theories, that the propagating steps involved a chain reaction which produced either an aldehyde or a peroxide and that branching occurred due to further reaction of the aldehyde or peroxide, has, until recently, been the basis of all hydrocarbon oxidation mechanisms. The relative merits of these two theories are discussed below.

a) Peroxide Theories and Evidence for Peroxides in Oxidation Systems.

Walsh [18] supported the theory of peroxide branching proposed by Ubbelohde but stressed that rupture of an adjacent C-C bond was likely to occur in addition to breaking of the O-O link. An additional degradation step was introduced by Walsh to explain the degradation of the fuel molecule.

i.e. Branching $ROOH = RO + OH$

Degradation $RO = R' + HCHO$

The peroxide theory was favoured by several other workers as it was thought that it provided an explanation of why so many products of hydrocarbon oxidation contained only one oxygen atom and of the dependence of the rate of oxidation on the structure of the molecule.

Hinshelwood [19] and Cullis, Hinshelwood and Mulcahy [20] suggested that the rate of oxidation was dependent on the strength of the O-O bond in the peroxide and that the strength of the O-O bond was dependent on the substituent groups in the peroxide molecule. As a result of this bond strength difference, hydrocarbons were oxidised at different rates. This conclusion has since been proved to be false as the O-O bond strength has been shown to be independent of the structure of the peroxide. [21]

If peroxides do in fact act as branching intermediates, their presence should be detectable in oxidation products. In oxidations in solution, where the temperature is low and the hydrocarbon concentration high, evidence exists for the formation of peroxides. [22] However, in gas phase oxidations, which must take place at higher temperatures, there is much less evidence for the existence of peroxides other than hydrogen peroxide.

Using a catalyst such as hydrogen bromide, gas phase oxidations have been carried out at temperatures as low as 125°C - 170°C. Rust and Vaughan [23] and Allen and Tipper [24] have investigated the hydrogen bromide catalysed oxidation of isobutane and have found that 80% of the oxygen consumed results in t-butyl-hydroperoxide. When ethane [25] and propane [26] were similarly oxidised, no primary or secondary hydroperoxides were formed. A similar picture has been obtained as a result of uncatalysed oxidations at temperatures some 100°C or so higher. Using paper chromatography to isolate and detect hydroperoxides formed in the oxidation of propane at 327°C, the oxidation of n-heptane between 250°C and 270°C and the oxidation of n-butane between 315°C and 345°C, Cartlidge and Tipper [27] found that with n-heptane and n-butane

the peroxidic material isolated consisted of a mixture of hydroperoxides, hydrogen peroxide and hydrogen peroxide - aldehyde adducts but with propane only hydrogen peroxide and its derivatives were detected. From these results, Cartlidge and Tipper concluded that, although they may act as branching agents in the oxidation of higher hydrocarbons, hydroperoxides could not act as branching agents in the oxidation of the lower hydrocarbons. This work supported the view of Kirk and Knox [28] that at 318°C the lifetimes of ethyl and propyl hydroperoxides were too short for them to be the intermediates responsible for degenerate branching in ethane and propane oxidations above about 300°C.

In a study of the oxidation of propane, Seakins [29] showed that coating the reaction vessel with potassium chloride, while reducing the overall rate of reaction, did not affect the ratio of reaction rate to peroxide concentration. The change in surface did not alter the primary chain length but destroyed the peroxide which was identified as the branching agent. The conclusions of this work are doubtful as the uncharacterised peroxide is likely to have been mainly hydrogen peroxide which is inactive as a catalyst.

With the higher hydrocarbons, no conclusive evidence is available that peroxides can act as the branching intermediates although peroxides have been detected in such oxidation systems. A major difficulty has been the lack of suitable analytical techniques for the isolation and identification of the hydroperoxides formed in the systems. Batten, Gardner and Ridge [30] used polarography to analyse the peroxides formed in the oxidation of isobutane between 250°C and 270°C and, although this was one of the more refined analytical techniques then available, they could not definitely establish that t-butyl-hydroperoxide was formed. Taylor [31], using paper chromatography, was later able to show that t-butyl hydroperoxide was formed in the system up to temperatures of 350°C.

The destruction of peroxides formed during the course of a reaction has been used to show that peroxides cannot act as branching agents. Batten and Ridge [32] found that destruction of peroxides by withdrawing the products formed in the oxidation of isobutane into a vessel containing mercury had no effect on the subsequent reaction as the reaction continued at the same rate as before interruption when the products were restored to the reaction vessel. The above method has also been used in the oxidation of propane and propylene by Shtern [33] and by Pease [34] for propane oxidation to demonstrate that peroxides were not the agents of degenerate branching.

b) Aldehyde Theory.

As early as 1929, the importance of aldehydes in hydrocarbon oxidation was recognised by Pope, Dykstra and Edgar [35] who suggested that hydrocarbons were oxidised via aldehydes which were degraded step by step to lower aldehydes.

$$RCH_2CHO + O_2 = RCHO + CO + H_2O = \cdots = HCHO + CO + H_2O$$

Since this theory did not produce formaldehyde in an excited state as required for cool flames and as the higher aldehydes could be detected in only certain cases, this theory was modified by Lewis and Von Elbe [36] to a scheme whereby radicals were degraded instead of molecules.

$$RCH_2CO + O_2 = RCO + CO + H_2O = \cdots = CH_3CO + CO + H_2O$$

By postulating a different reaction for CH_3CO than for the higher radicals, namely $CH_3CO + O_2 = CH_2O + CO + OH$, Lewis and Von Elbe could explain the formation of excited formaldehyde as this reaction is exothermic to the extent of 110k cal. An additional advantage of this scheme was that a "straight through run" could now be envisaged which would account for the predominance of formaldehyde over the other aldehydes in the reaction products.

In 1948, Norrish [37], after several modifications of his atom chain scheme for oxidations, proposed a scheme for higher hydrocarbon oxidation in which OH radicals carried the propagating steps and which also contained a degradative reaction involving the successive formation and destruction of RCH_2CO radicals which were thought to have only a transitory existence.

Propagation	$RCH_2CH_3 + OH$	=	$RCH_2CH_2 + H_2O$
	$RCH_2CH_2 + O_2$	=	$RCH_2CHO + OH$
Branching	$RCH_2CHO + O_2$	=	$RCH_2COOH + O$
Degradation	$RCH_2CHO + OH$	=	$RCH_2 + CO + H_2O$
	$RCH_2 + O_2$	=	$RCHO + OH$
	$RCHO + OH$	=	$R + CO + H_2O$
	. . . . .		. . . . .
	$CH_3CO + O_2$	=	$CH_2O + CO + OH$

Branching in this reaction scheme was due to the reaction of aldehyde with oxygen producing oxygen atoms which were capable of initiating fresh chains.

While there are small differences within each of the two groups of theories, the main difference between the two theories is clear. In both theories, the hydrocarbon is initially attacked by oxygen to form an alkyl radical which in turn combines with oxygen to form an alkyl peroxy radical. According to the Peroxide Theory, the alkyl peroxy radical is sufficiently stable to undergo reaction with an other molecule of hydrocarbon before decomposition occurs.

i.e. $RCH_2OO + RCH_3 = RCH_2OOH + RCH_2$

In the Aldehyde Theory, the alkyl peroxy radical is thought to be very unstable and decomposition occurs at once to give an aldehyde and an OH radical.

i.e. $RCH_2OO = RCHO + OH$

Degenerate branching is controlled by decomposition of the peroxide in the first case and by reaction of aldehyde in the second. Increase in temperature will favour the decomposition of the alkyl peroxy radical and it is reasonable to suppose that an aldehyde mechanism will operate at high temperatures and a peroxide mechanism will take part at lower temperatures. As there is no doubt about the presence of aldehydes and of their ability to act as branching intermediates in hydrocarbon oxidations around 300°C, the Aldehyde Theory is favoured.

Usually less than 10% of the hydrocarbon consumed was converted to aldehydes and to explain this it was suggested that aldehydes themselves were oxidised very rapidly. Although such reaction may occur, the existence of an alternative path for the reaction of alkyl radicals with oxygen could account for the low yields of aldehydes.

i.e. $R + O_2 \rightarrow R'CHO + OH$

$R + O_2 \rightarrow$ other products

The idea that peroxide and aldehyde formation may not be the main way of reaction of alkyl radicals and oxygen has gained prominence in recent years.

c) HO_2 radical theory.

Recently, evidence from oxidations carried out at high temperatures has led to the conclusion that oxygen can react with an alkyl radical to form an olefin. Satterfield and Wilson [38], Satterfield and Reid [39], and Knox [40] found high yields of propylene in the reactions of oxygen with propane and propyl radicals while Gray [41] detected considerable amounts of ethylene in ethane oxidation. It was suggested that these high temperature oxidations proceeded by an HO_2 radical mechanism.

e.g. $C_nH_{2n+1} + O_2 = C_nH_{2n} + HO_2$ (1)

$C_nH_{2n+2} + HO_2 = C_nH_{2n+1} + H_2O_2$ (2)

Although little direct evidence has been put forward for the existence of HO_2 radicals in hydrocarbon oxidation systems, a great deal of indirect evidence supports this view. Mass spectrometric evidence has been found in the oxidation of methane [42], in which CH_3 and HO_2 are the first products of reaction and H_2O_2 is formed at a later stage, and methyl radicals [43]. Large amounts of hydrogen peroxide have been found in methane and propane oxidations, the hydrogen peroxide in propane oxidation possibly being formed by reaction (2) above. Walsh and his collaborators [44] identified the active anti-knock agent from tetra-ethyl lead as lead dioxide and suggested that HO_2 was one of the likely chain carriers being destroyed. Further evidence for the existence of HO_2 has come from the work of Baldwin et al.[45] on the hydrogen - oxygen reaction in a boric acid coated vessel. The kinetic features of the reaction i.e. the variation of the rate of the slow reaction with mole fraction of reactants and the nature of the second explosion limit have been successfully explained by a mechanism involving the combination of two HO_2 radicals to give hydrogen peroxide, the bimolecular decomposition of H_2O_2 being responsible for the autocatalytic nature of the reaction.

i.e. $HO_2 + HO_2 = H_2O_2 + O_2$ (10) (the equations are numbered

$H_2O_2 + M = 2OH + M$ (7) as in Baldwin's papers)

It has been suggested that HO_2 radicals also take part in alcohol oxidations. During the oxidation of ethanol at temperatures between 250°C and 270°C, Cullis and Newitt [46] found that under optimum surface conditions, acetaldehyde and hydrogen peroxide were produced to equivalent yields and they considered that this result was in agreement with the following mechanism:

$$C_2H_5OH + HO_2 = C_2H_4OH + H_2O_2$$

$$C_2H_4OH + O_2 = CH_3CHO + HO_2$$

Similar results were found for the oxidation of n- and iso- propanol [47-48] and of n-, sec-, iso- and tert- butanol[49]. In each case, only hydrogen peroxide and a single oxygenated compound initially resulted. Evidence was put forward that, as in alkane oxidation, the autocatalytic nature of the reaction was due to the reaction of an intermediate. For example, the oxidation of isopropanol resulted in the formation initially of only acetone and hydrogen peroxide. A small proportion of the iso-propyl radicals formed resulted in the formation of acetaldehyde, the oxidation of which resulted in autocatalysis and the formation of methanol, formaldehyde, glyoxal, and carbon monoxide as minor products.

In much early work on oxidations, analytical methods necessitated the use of large amounts of reaction products for analysis. As a result, only the later stages of hydrocarbon oxidations could be examined. Using such methods, the low temperature oxidations of hydrocarbons seemed to result mainly in the formation of oxygenated compounds. Hence, it was thought that the HO_2 radical mechanism did not operate in this region. Through the development of gas chromatography, the initial stages of oxidations can now be examined in greater detail and Knox[50], Knox and Wells [51] and Zeelenberg and Bickel [52] studying propane, ethane and isobutane oxidation respectively, have shown that, in the initial stages of the low temperature reaction, 75-80% of the alkane consumed is converted to the corresponding olefin. These results indicate that the HO_2 radical chain also plays a part in low temperature oxidations at about 300°C.

Although the existence of an HO_2 radical chain in alkane oxidations seems well established, the lifetime of the chain carrying HO_2 radical is not accurately known. Minkoff [53], who reviewed the earlier evidence for its existence in oxidation systems, suggested that the HO_2 radical was a relatively long lived intermediate but did not give a value for its lifetime and it was not until Lewis and Von Elbe estimated the lifetime of HO_2 in the hydrogen - oxygen systems, under conditions similar to those used in hydrocarbon oxidations, to be 1 sec that an idea as to the length of its lifetime was obtained.

The general view is that, during the initial stages of the reaction, 80% of the alkyl radicals react by the HO_2 radical chain mechanism to form an olefin while the remaining 20% cause branching reactions by means of either the aldehyde or the peroxide mechanism.

2. Slow Oxidation of Isobutane.

Isobutane oxidation is of interest as isobutane has a weak C-H bond at which oxygen attack should preferentially take place and as the resulting hydroperoxide, t-butyl hydroperoxide, is relatively stable. Studies on isobutane oxidation may be used to test the theory that hydroperoxides act as the branching intermediates in hydrocarbon oxidations. Isobutane oxidation has been studied in flow and static systems. Until recently, flow systems were more useful than static systems for product analyses as large amounts of products could be collected. Static systems are more suitable than flow systems for examination of kinetic parameters.

The characteristics of the non explosive oxidation of propane and the butanes were studied by Pease [54] using a flow system. Only gaseous products were analysed. In the temperature range 300 - 625°C, the principal products were found to be CO and unsaturates, CO_2 and H_2 rarely being important products. Wall effects were observed and Pease found that packing the reaction vessel caused the inhibition of the oxidation of propane below 500°C. Coating the reactor with potassium chloride was found to raise the minimum temperature at which propane oxidation took place to 575°C.

Catalysed oxidations generally take place at considerably lower temperatures than uncatalysed oxidations and result in higher conversions of reactants. Ozone and HBr have been used as catalysts in isobutane oxidation. Rust and Vaughan [23] showed that in the presence of HBr, ethane was converted to mainly acetic acid, straight chain compounds were converted to ketones and branched chain compounds were converted to hydroperoxides. Introduction of oxygen under these conditions was accompanied by a low degree of C-C scission. For example, Rust and Vaughan found that at 163°C, 70% of the isobutane consumed in a flow system was converted to t-butyl hydroperoxide. As the flow system results were

shown to be surface sensitive, surface effects were studied in a static reactor. 75-85% yields of t-butyl hydroperoxide were obtained in a boric acid coated vessel but hydroperoxide yields were lower in a clean vessel due to surface decomposition of the hydroperoxide. Similar results were obtained by Allen and Tipper [24] who showed that, below 170°C in a static system using a boric acid coated reactor, the overall process up to 70% reaction was mainly

$$(CH_3)_3CH + O_2 \quad = \quad (CH_3)_3COOH$$

the pressure decrease being a measure of the extent of the reaction. Above 170°C, the pressure dropped to a minimum and then rose due to decomposition of the hydroperoxide formed. Autocatalysis was thought to be due to the reaction of a small proportion of the t-butyl peroxy radicals with HBr to give radicals. The main chain carriers were bromine atoms and t-butyl peroxy radicals, the former abstracting hydrogen from isobutane and the latter abstracting hydrogen from HBr in the propagating steps.

i.e. in the temperature range below about 150-160°C.

Branching	$(CH_3)_3COOH + HBr$	=	Br + other products	(1)
Propagation	$Br + (CH_3)_3CH$	=	$HBr + (CH_3)_3C$	(2)
	$(CH_3)_3C + O_2$	=	$(CH_3)_3COO$	(3)
	$(CH_3)_3CO_2 + HBr$	=	$(CH_3)_3COOH + Br$	(4)
Termination	$(CH_3)_3COO + Br$	=	$(CH_3)_3COOBr$	(5)

On a clean surface, rapid decomposition of hydroperoxide occurred at the walls. Hydrogen bromide catalysed the reaction in two ways. As it contains an easily removed H atom, hydrogen bromide enabled the chain to be propagated (equation (4) above) and assisted branching by reacting with the hydroperoxide (equation (1) above).

Cullis, Fish and Ward [55] reached similar conclusions as a result of study

of the effects of HBr and four bromomethanes (CH_3Br, CH_2Br_2, CH_2ClBr, and CF_2Br_2) on the slow combustion of organic fuels such as formaldehyde, ethane, acetaldehyde, isopentane and isopropanol. Organic bromine compounds had a pronounced effect on the reation only under conditions in which they themselves were converted to HBr or Br_2. Promotion by HBr appeared to be ascribable either to its direct reaction with oxygen providing an extra, more effective mode of chain initiation or to its interaction with intermediate peroxides giving rise to enhanced chain branching.

Ozone catalysed oxidations carried out by Schubert and Pease [56] in the range 110°C to 270°C showed that at around 265°C the ozone induced reaction merged with the normal uncatalysed reaction. At 150°C, t-butyl hydroxy methyl peroxide which was detected by infra-red spectroscopy in normal oxidations at 270°C was the major product. Although it was proposed that O_3 might be the branching agent in normal combustion as a result of the reaction,

$$RO_2 + O_2 = RO + O_3$$

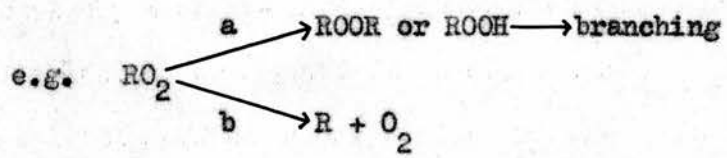
no ozone could be detected in normal combustion. In addition, no ozone has been detected after flash photolysis of azomethane in the presence of oxygen [57] although methyl peroxy radicals were undoubtedly formed.

Extensive studies of isobutane oxidation in a static system at 291°C by Batten, Gardner and Ridge [58] resulted in accumulation of data for the consumption of reactants and formation of products during the oxidation. During the induction period, which was defined as the time taken for the rate of reaction to reach 0.5mm pressure rise per minute, appreciable quantities of reactants were converted into products. A difference in the distribution of products during and after the induction period was thought to be due to reaction by

straight chains during the induction period. Experiments, which were interrupted at an intermediate stage in the reaction in order to destroy peroxides by contact with mercury, showed that alkyl hydroperoxides were not the intermediate responsible for branching as such interrupted reactions continued at the same rate as before interruption on return to the reaction vessel. Evidence was also put forward that the branching agent, once formed in sufficient quantity, caused the reaction to proceed irrespective of the condition of the surface. The rate of reaction was increased by the addition of acetaldehyde and t-butyl hydroperoxide and decreased by the addition of formaldehyde, water and formic acid. Inert gas reduced the induction period but had little effect on the maximum rate. This result suggested that although the length of the induction period was controlled by the destruction of an active intermediate at the wall, the effects of surface were of secondary importance after the end of the induction period. Although product/time graphs showed that formaldehyde, higher aldehyde and total peroxide yields passed through maxima at the maximum rate of pressure rise, no conclusion could be drawn as to the nature of the branching intermediate.

Advances in analytical techniques, in particular gas chromatography and mass spectrometry, enabled Bose [59] to carry out more detailed product analyses over the temperature range 290-390°C in a static system. As he considered that di-t-butyl peroxide was a possible branching agent, Bose studied the effects of di-t-butyl peroxide premixed with isobutane, di-t-butyl peroxide premixed with oxygen, and the oxidation products of di-t-butyl peroxide on the oxidation of isobutane. All additives had little effect on the maximum rate of reaction although all, with the exception of formaldehyde, decreased the length of the induction period. Bose compared the oxidation products of isobutane and

di-t-butyl peroxide at high (390°C) and low (290° C) temperatures and concluded that different mechanism of isobutane oxidation operated at the two temperatures. The anomalous temperature coefficient in the oxidation of isobutane was related to the increasing dissociation of a radical RO_2 responsible for branching. At low temperatures, the radical RO_2 was relatively stable and could lead to branching by reaction (a) but as the temperature rose the radical dissociated by (b).



As the stability of the RO_2 radical decreased, the high temperature reaction dominated.

A more detailed investigation of isobutane oxidation has been carried out by Zeelenberg and Bickel [52] who used flame ionisation detection and gas chromatography to analyse the products. Over a considerable range of temperature and mixture composition, the relative yields of products were unaltered by change of temperature and mixture composition. They supposed that products were formed by intramolecular decomposition of iso-butyl peroxy and t-butyl peroxy radicals. Zeelenberg and Bickel showed that the primary products (isobutane, propylene, acetaldehyde, propionaldehyde, acetone, methanol, isobutene oxide) were formed according to the equation $C = C_o e^{\phi t}$, that the net branching factor ϕ was constant for all primary products and that initially 80% of the isobutane consumed was converted to isobutene.

Taylor [31] investigated the formation of peroxides in isobutane oxidation over the range 250-370°C in a flow system at atmospheric pressure using a 1:1 isobutane: oxygen ratio. Liquid products were condensed at - 90°C and

analysis for peroxides carried out by paper chromatography. At 250°C, t-butyl hydroperoxide predominated although hydrogen peroxide was also formed. At 360°C, only hydrogen peroxide was detected. Taylor concluded that t-butyl hydroperoxide was the main peroxidic product of the induction period although hydrogen peroxide was also formed.

Isotopic tracer techniques have been used to determine the mode of formation of ketones in isobutane oxidation [60]. Addition of 1:3 ^{14}C acetone to reaction mixtures of isobutane and oxygen has established that none of the methyl ethyl ketone formed in the cool flame region and only one quarter of that formed in slow oxidation arose from further reaction of acetone. The formation of methyl ethyl ketone probably involved rearrangement and subsequent decomposition of the t-butyl peroxy radical. The above work is an example of the use of a ^{14}C labelled intermediate to distinguish between an intermediate (acetone) and the fuel molecule (isobutane) as the origin of a product (methyl ethyl ketone). The route by which product formation occurs can also be determined if the fuel molecule is labelled with ^{14}C in a particular skeletal position and the concentration and site of the labelled isotope in this product is then determined. Tracer studies on the slow combustion of 2-methyl pentanes [61] labelled in each skeletal position in turn have shown that CO is derived principally from the 3 and 4 positions while the 2-carbon atom of 2-methyl pentane was shown to be the 2 carbon atom of acetone. The point of initial oxidative attack can be determined by labelling each C atom in turn and measuring the isotopic enrichment of the fuel products in each case as has been done for 2-methyl pentane [61]. By measuring the H/D ratio in the water formed from the oxidation of five deuterated propanes, Burt, Cullis, Larsen and Minkoff [62] have shown that the rate of removal of H from a secondary C atom was twice

the rate of removal of H from a primary C atom. These examples illustrate the value of isotopic tracer technique in elucidating oxidation mechanisms.

This review shows that isobutane oxidation has been investigated over a wide range of conditions. The mechanism of the low temperature hydrogen bromide catalysed oxidation has been reasonably well established. The nature of the branching intermediate in the uncatalysed oxidation is uncertain and, although recent work which was published after the present work had started indicates that an HO_2 radical chain mechanism operates in the low temperature region, the mode of formation of the minor products, aldehydes, ketones, epoxides and alcohols has not been firmly established.

3. Surface Effects in Hydrocarbon Oxidations.

Irreproducibility of reaction rates is one of the phenomena of hydrocarbon oxidation which is due to the effect of changes in the condition of the reaction vessel surface. The kinetic parameters most affected by surface conditions are the length of the induction period, τ, and the maximum rate of reaction. Many workers [63] have noted that new reaction vessels required "conditioning" before reproducible results could be obtained. Differences in reaction rates are thought to be due to the differences in the efficiences of the reaction vessel walls in destruction of the chain carrying radicals.

The effect of surface has also been demonstrated by increasing the surface area of the reaction vessel while altering the volume slightly [64-5]. Reaction rates have been greatly decreased by this process and in some cases complete inhibition has occurred. In a series of experiments on hydrocarbon oxidation in reaction vessels of constant volume but differing diameters, Norrish and Reagh [66] showed that, when the diameter of the reaction vessel was sufficiently small, the reaction rate dropped to zero and the induction period tended to infinity. In narrow vessels, surface deactivation could predominate over other deactivation processes although in wider vessels surface and volume deactivation occurred to a comparable extent over a considerable pressure range.

Coating of the reaction vessel with inorganic compounds markedly affects the reaction kinetics. On acidic surfaces which are brought about by coating with boric acid or by washing the reaction vessel with a solution of hydrogen fluoride [67], the induction periods are decreased and maximum rates are increased but the reverse is generally true on salt or oxide coated surfaces (i.e. sodium chloride, potassium chloride, sodium hydroxide, lead oxide). Salt surfaces are very active destroyers of radicals and during oxidations in salt coated vessels

the effect of inert gas on the length of the induction period and the maximum rate is most marked. With acidic surfaces, the effect of added inert gas is not so noticeable.

Broatch, McEwan and Tipper [68] studied cyclopropane oxidation and considered that changes of rates of reaction on various surfaces were due to different proportions of HO_2 radicals being heterogeneously removed. That acidic surfaces increased the rate of reaction and that alkali coatings were retarders was illustrated by the rate of oxidation in a boric acid coated vessel being 140 times faster than that in a sodium hydroxide coated vessel. Similar effects were observed by Bell and Tipper [69] during the oxidation of methanol.

Reaction products may also be destroyed at the walls of the reaction vessel. Peroxides, which are particularly susceptible to decomposition, decompose to a greater degree in salt coated vessels than in vessels with acidic surfaces [70]. High yields are generally only obtained on acidic surfaces which preserve peroxides.

As a result of work on methane oxidation at 500°C in a silica reaction vessel, Walsh et al.[71] have divided surfaces into two categories: 1) acidic surfaces on which the reaction rate varies little from one acidic surface to another and 2) salt surfaces on which the rate of reaction differs greatly from acidic surface reaction rates and from one salt surface to another. The difference in the rate of oxidation of methane has been explained in terms of the different fates of HO_2 radicals on different surfaces. On a type 1) surface HO_2 reacts in a manner similar to that in acid solution.

i.e. $$HO_2 + H^+ \longrightarrow \tfrac{1}{2}H_2O_2 + \tfrac{1}{2}O_2 + H^+ \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

On a type 2) surface, the reaction would be

$$HO_2 + e \longrightarrow \tfrac{1}{2}H_2O + \tfrac{3}{4}O_2 + e \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

Walsh postulated a link between the effectiveness of surface 2) as an inhibitor and simple expectations as to availability of surface electrons for donation. Inhibiting efficiency should increase from NaCl to KCl to CsCl and from KF to KCl to KBr to KI and no exception to this rule was known. The wide variety of observed effects could not be explained on the basis of only one chain carrier and, as H_2O_2 should be observed on type 2) surfaces as $HO_2 + CH_4 = H_2O_2 + CH_3$ is considerable, Walsh proposed a reaction to explain the decomposition of H_2O_2 on type 2) surfaces.

i.e. $H_2O_2 + e \longrightarrow H_2O + \frac{1}{2}O_2$

Such a scheme explained both surface and kinetic effects.

Initiation reactions for some oxidation reactions have been put forward as bimolecular surface reactions but little work has been done on the variation with surface conditions of the yields of products other than peroxides.

Satterfield and Reid [72] have carried out propane oxidation in a flow system using reactors of different surfaces. Yields of products obtained using a special reactor which minimised surface effects were compared to yields in a normal type reactor using different surfaces. A plot of ratio of product yield for the modified vessel to product yield for the Pyrex vessel against the ratio, ϕ, of peroxide formed to propylene formed for the same surfaces gave an indication of surface dependent products assuming that activity in decomposing H_2O_2 paralleled the extent to which surfaces participated in other wall reactions. Propylene and methanol were found to be products of gas phase reactions whereas ethylene was thought to be formed on the surface by the reaction.

$C_3H_7 \longrightarrow C_2H_4 + CH_3$

Although chain initiation and chain termination steps have for some time been considered to take place at the walls of the reaction vessel, there is very little data on the extent to which propagation steps involve surface processes.

4. Aim of the Research.

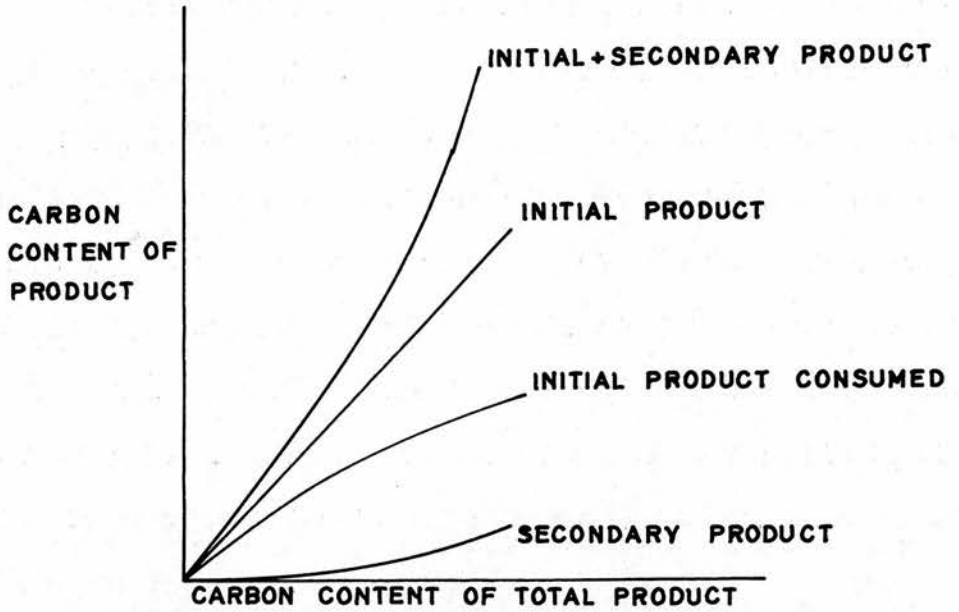
To account for the existence of a negative temperature coefficient in hydrocarbon oxidation, it had been assumed that different reaction mechansims operated in the low (less than 350°C) and high (greater than 400°C) temperature regions. Product analysis carried out in the later stages of reactions showed that oxygenated compounds were the main products of low temperature oxidation while olefins were the main products of high temperature oxidation. Through the application of more sensitive analytical techniques to the initial stages of oxidations, olefins have been shown to be the main initial products of the low temperature oxidation of ethane and propane. An HO_2 chain mechanism has been proposed, e.g. for propane

$$C_3H_7 + O_2 = C_3H_6 + HO_2$$

$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2$$

The aim of the present work was to investigate the low temperature oxidation of isobutane in order to determine whether or not the initial stages of isobutane oxidation also involve an HO_2 radical chain mechanism. It was proposed to follow, using gas chromatography for product analyses, the product formation and reactant consumption throughout the course of the reaction. The effects of variation of reaction temperature and hydrocarbon/oxygen ratio were to be investigated. Katharometer detection was proposed for the gas chromatographic analyses as this method is most suitable for the determination of oxygen, methane and carbon oxides. By plotting the yields of individual products against the total product yield in mm atoms carbon, it was hoped to distinguish between initial and secondary products. As total product formation increases, the fractional yields of primary products should fall below their initial gradients whereas the fractional yields of secondary products should rise above their

initial gradients. These features are illustrated in the figure below.



As the oxidation of isobutane was likely to yield a complex mixture of products many of which would be more reactive than the parent alkane, primary processes were likely to be obscured by the oxidation reactions of primary products during the later stages of the reaction. For this reason, it was intended to study the oxidation at very low alkane conversion using more sensitive analytical techniques. Using flame ionisation detection, extremely small amounts of products can be detected. Thus, studies at low percentage conversion should be able to isolate the primary reactions and yield a clearer picture of the reaction mechanism. The effects of variation of temperature and mixture composition were again expected to yield valuable indications of the reaction mechanism. If products are formed from the same source (and the products of oxidations are accepted as being formed from reactions of alkyl peroxy radicals), the ratios of the initial rates of formation of the products at various temperatures can be used to calculate the activation energy differences and the A factor ratios of pairs of competing reactions.

for example, if RO_2 $\xrightarrow{k_1}$ Product X ..... (1)

$\xrightarrow{k_2}$ Product Y ..... (2)

$$\text{then } \frac{\text{Rate of formation of X}}{\text{Rate of formation of Y}} = \frac{K_1}{k_2} = \frac{A_1}{A_2} \times \frac{e^{-E_1/RT}}{e^{-E_2/RT}}$$

where A_1, A_2 and E_1, E_2 are the A factors and activation energies of the respective reactions.

$$\therefore \log_e \frac{\text{Rate of formation of X}}{\text{Rate of formation of Y}} = \log_e \frac{A_1}{A_2} + \frac{(E_2 - E_1)}{RT}$$

Hence, if log (ratio of rate of formation) is plotted against $^1/T$ the slope of the line gives the activation energy difference between (1) and (2) and the intercept yields a value for the A factor ratio.

After preliminary experiments had shown that initially 80% of the alkane was converted to olefin, a study of competitive oxidation of propane and isobutane was carried out to try to confirm that the radical attacking the hydrocarbon was HO_2.

i.e. $RH + HO_2 \longrightarrow R + H_2O_2$ ($R = C_2H_5$, C_3H_7 or C_4H_9)

The bond strength D [H - OOH] is now firmly established as 89 k.cal. [73] and most of the abstraction reactions of HO_2 with the above H donors will be endothermic and the selectivity of HO_2 should be similar to that of a bromine atom. If this

is the case, the results of the competitive experiments of Knox, Falconer and Trotman-Dickenson [74] are difficult to explain. They found that the selectivity of the attacking radical in mixed oxidations was between that of Cl and CH_3 but much less than that of Br and they suggested that the attacking radical might be OH. Knox et al. derived their relative rate constants from the relative consumptions of the mixed hydrocarbons, a process which requires at least 10% reaction and is not as accurate as the method proposed below. If competitive experiments are carried out with propane and isobutane and if both hydrocarbons give about 80% initial conversion of the hydrocarbon to the corresponding olefin, the relative rate constants for the attack of the propagating radical on the two hydrocarbons is given to a good approximation by

$$\frac{k \text{ iso } C_4H_{10}}{k\, C_3H_6} = \frac{[iC_4H_8]\,[C_3H_8]}{[C_3H_6]\,[iC_4H_{10}]}$$

where the olefin concentrations are found by gas chromatographic analysis and the hydrocarbon ratios are those in the initial mixture.

The validity of the above expression depended on the assumption that each alkane yielded the same percentage of olefine. To verify this, it was necessary to carry out some propane oxidations to determine the initial yields of propylene and oxygenated compounds.

As, during the course of some experiments at 330°C, peculiar effects were noted which were possibly due to surface effects, a series of oxidations was carried out using different reaction vessel surfaces to determine the exact nature of the effect of surface on product yields.

EXPERIMENTAL TECHNIQUE

1) Apparatus

Although the apparatus used was essentially a unit, it is useful for descriptive purposes to divide it into three sections: a) General Apparatus b) Kinetic Apparatus c) Analytical Apparatus.

1.1. General Apparatus

Pumping and Storage System

The Pyrex glass pumping system was of conventional design (figure 1), an Edwards High Vacuum Rotary Pump backing a two stage mercury diffusion pump. Pressures of 10^{-5} - 10^{-6} mm Hg were obtained and were measured on a vacuostat. Reactants were stored in five - litre bulbs and detachable traps were used for the insertion of other compounds. Mixtures were made up in a 1 litre mixing vessel. Greased stopcocks were used through this section of the apparatus.

Reaction Vessel

A spherical Pyrex reaction vessel, diameter 11 cm and volume 600 ml was used. A 0.5 mm capillary probe was sealed into the reaction vessel for removal of samples (figure 1). Before being fused to the apparatus, the reaction vessel was thoroughly washed with chromic acid and rinsed with distilled water.

Temperature Measurement

The reaction vessel temperature was measured by a T_1/T_2 thermocouple (British Driver Harris Ltd.) which had a calibration supplied, in conjunction with a Doran D.C. potentiometer. The reference temperature was $0^{\circ}C$.

Furnace

The furnace consisted of a silica tube, 46 cm in length and 12 cm internal diameter, which was heated by three independent windings of nichrome wire of

resistances, 20, 48 and 20 ohms, the whole being suitably lagged and insulated. The temperature difference along the furnace was kept at less than 2°C by shorting out the centre winding. Temperature control to ± 1°C was achieved using a Sunvic R.T.2 Temperature Controller and platinum resistance thermometer. The furnace circuit is shown in figure 2.

1.2. Kinetic Apparatus.

The pressure change in the reaction vessel was measured using a differential pressure transducer (J. Langham Thomson, Herts - Type U.D.P.3) which was connected to the reaction vessel through 2.5 mm Pyrex capillary. The transducer operated on the Wheatstone Bridge Principle, a difference in pressure between the positive and reference sides of the transducer resulting in an out of balance E.M.F. The input voltage was supplied by six 2 volt accumulators and was maintained at 10 volts by means of a variable resistance. All capillary leads were heated using nichrome wire heated to a temperature sufficient to prevent condensation of any products which might diffuse into the leads. The transducer was housed in a vacuum tight desiccator in which the reference pressure could be adjusted so that the out of balance E.M.F. was less than 1 mV. During runs, the increase in the out of balance E.M.F. was counterbalanced by a Doran D.C. potentiometer so that the net out of balance E.M.F., measured on a Honeywell Brown 1 mV recorder, was always less than 1 mV. A change of 1 cm in pressure on the positive side of the transducer resulted in a 1 mV change in output. Thus, the pressure could be measured to 0.02 mm Hg. The transducer was calibrated by measuring the deflection of the recorder pen in mm distance travelled on the recorder chart against the change in pressure using a mercury manometer. Forty observations were made and the mean calibration factor was 1 mm chart distance = 0.0387 ± 0.0003 mm Hg.

1.3. Analytical Apparatus.

1. Sampling System.

a) for runs in which H_2O_2 and HCHO were not determined.

The sampling system consisted of ten Pyrex bulbs of approximate volume 1.8 ml connected to each other and to the reaction vessel by a manifold of 0.5 mm Pyrex capillary tubing which was heated to prevent condensation. Greaseless valves (F.J. Hone and Co., London) were used throughout this system to prevent solution of products in tap grease. Glass metal connections were made using Araldite (C.I.B.A. Ltd., Cambridge).

b) for formaldyhyde determinations.

When formaldyhyde determination was required, the system was altered so that only three detachable bulbs of volume approximately 4 ml were used. In both the above systems, the volumes of the bulbs were accurately determined by filling each in turn with air at a known temperature and pressure. The gas from each bulb was measured in a gas burette and the volumes of the bulbs calculated.

c) for Hydrogen Peroxide determination.

In this case, the sampling system consisted of a 100 ml detachable Pyrex cylinder connected to the reaction vessel through a greased stopcock to eliminate possible decomposition of hydrogen peroxide on metal valves.

2. Toepler Pump.

Non-condensable gases were measured in a Toepler Pump whose bulbs had volumes 11.38 ml, 3.98 ml and 0.851 ml respectively. A glass injection system with two way stopcocks was used in conjunction with the Toepler Pump.

3. Chromatography Injection System.

The injection system was a Pyrex U tube of volume 3.010 ml connected by means of Hone valves to the vacuum line, carrier gas supply, sample system and reaction vessel (figure 3). Injections were made by opening taps (2) and (4) before tap (3) in order to minimise back diffusion of any non-condensable product.

4. Carrier gas.

Hydrogen was used as carrier gas in all analyses. When a katharometer is used as detector, hydrogen as carrier gas has the advantage of greater sensitivity and greater baseline stability. Since thermal conductivity is $\propto 1/\sqrt{M.W.}$, hydrogen has a greater thermal conductivity than nitrogen and thus a greater detector response is obtained using hydrogen as carrier. As the chromatography columns used for this work were generally long (15-25 ft.), hydrogen had an additional advantage as flow rates of the order of 30 ml/min could be obtained using lower pressure drops across the column than were necessary to obtain similar flow rates of nitrogen. The only disadvantage of hydrogen other than its explosion risk is that the column efficiency is less using hydrogen than it is using nitrogen as carrier. Hydrogen was supplied from a B.O.C. cylinder through a two-stage reducing valve and dried by passage through a tube of activated Molecular Sieve 13X. Buffer vessels were used to minimise variations of flow rates and fine control was obtained by an Edwards High Vacuum needle valve, Type OSC1.

5. Gas Chromatography Columns.

4 mm internal diameter Pyrex tubing was used throughout. The table below shows the columns used for analysis with a) katharometer detection and b) flame ionisation detection.

Table 1. Columns used for Katharometer Detection

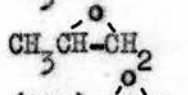
Column No.	Compounds Analysed	Length (ft)	Column Packing	Stationary Phase	Column Temperature	Flow Rate ml/min.
1	O_2, N_2, CH_4, CO	3	Linde Molecular Sieve 13X.	-	Room Temp.	25
2	C_2H_4, CO_2, C_3H_8 C_3H_6, i C_4H_{10} nC_4H_{10}, i C_4H_8	10	fosalsil (60-90) mesh	20% dinonyl phthalate	Room Temp.	25
		15	fosalsil (60-90) mesh	20% acetonyl acetone	Room Temp.	
3	CH_3CHO  $(CH_3)_2C(O)CH_2$ C_2H_5CHO CH_3COCH_3 $CH_2=C(CH_3)CHO$ CH_3OH	17	celite (60-80) mesh	7% polyethylene glycol + 3% dibutyl phthalate.	35°C	30

Table 1. Columns used for Katharometer Detection. (contd.)

Column No.	Compounds Analysed	Length (ft)	Column Packing	Stationary Phase	Column Temperature	Flow Rate ml/min.
4	$(CH_3)_3COOH$	5	celite(60-80)	20% dinonyl phthalate	76°C	33
5	H_2O	2.5	Teflon (40-60) mesh	2% polyethylene glycol	47°C	30

Table 2. Columns used with flame ionisation detection.

Column No.	Compounds Analysed	Length (ft)	Column Packing	Stationary Phase	Column Temp.	Flow Rate ml/min.
6	CH_3CHO, $CH_3CH\overset{O}{\diagdown}CH_2$	15	celite (60-80) mesh	8% polyethylene glycol	Room Temp.	30
	$(CH_3)_2C\overset{O}{\diagdown}CH_2$					
	C_2H_5CHO					
	$(CH_3)_2CHCHO$, CH_3OH,					
	CH_3COCH_3					
	$CH_2 = C(CH_3)CHO$					
7	C_2H_4, C_3H_8, C_3H_6	15	fosalsil (60-90) mesh	20% dinonyl phthalate	Room Temp.	25
	iC_4H_{10}, iC_4H_8					
	nC_4H_{10}	15	fosalsil (60-90) mesh	20% acetonyl acetone	0°C	

6. Detectors.

a) Thermal Conductivity Detector.

The thermal conductivity cell used was a Gow-Mac (Model No. 9285) hot-wire katharometer, the four hot wires forming the arms of a Wheatstone Bridge. The bridge voltage was supplied by four 2 volt accumulators, the bridge current being kept constant at 240 milliamps by means of a variable resistance. Reference gas passed over two diametrically opposite arms of the bridge while sample gas passed over the remaining two (figure 4). The system was so arranged that carrier gas flowed through the reference side of the katharometer, through the chromatography column and then through the sample side of the katharometer. Such a system avoided the use of a dummy column. When carrier gas alone flowed through both arms of the katharometer, a steady state existed until a product was eluted from the column and passed over the sample filaments, the subsequent changes in resistance of these filaments causing an out of balance current in the bridge circuit. This current was fed into a 1 mV Honeywell Brown recorder with attenuation such that the range of the recorder could be increased to 0-1000 mV.

b) Flame Ionisation Detector.

The detector was constructed in the departmental workshops and was modelled on that used by Desty [75] (figure 4). The jet was maintained at a potential of 400 volts and the collector at zero potential. Air was filtered through a sintered disc in the base of the cell and the twin hydrogen streams mixed just before entering the jet. An additional hydrogen stream was necessary as otherwise the flame tended to be extinguished when injections were made. The subsidiary hydrogen flow of 20 ml/min was taken from a B.O.G. cylinder by means of a two stage reducing valve, controlled by a needle valve (Edwards High Vacuum - type OSC1), passed through a tube of activated Linde Molecular Sieve 13X and

finally passed through 1 foot of 0.01 mm diameter nylon capillary to give a steady flow. Air, 1000 ml/min was similarly supplied from a B.O.G. cylinder but stabilisation by passage through nylon capillary was not necessary. The output signal was fed into a flame ionisation amplifier unit (supplied by Imperial Chemical Industries Ltd., Heavy Organic Chemicals Division) and the amplified signal fed into a 1mV Honeywell Brown Recorder. Attenuation by a factor of 20 was possible and the output resistance of the electrometer amplifier could be varied from 2×10^8 to 2×10^9 ohms. The 400 V input detector voltage was also supplied by the amplifier unit.

2. Analytical Methods.

1. Gas Chromatography.

Gas chromatography was used for the analysis of oxygen, carbon monoxide, methane, ethylene, carbon dioxide, propylene, isobutane, isobutene, acetaldehyde, propylene oxide, isobutene oxide, propionaldehyde, isobutyraldehyde, acetone, methacrolein, methanol, water and t-butyl hydroperoxide. The columns used were given in tables 1 and 2.

Calibration of katharometer.

Oxygen and carbon monoxide were calibrated by injecting known amounts of the gases, measured in a gas burette, onto the appropriate column under standard operating conditions (e.g. 25 ml/min H_2, 240 milliamp bridge current) and measuring the peak areas produced on the recorder chart. Peak areas, which were measured using a planimeter, were preferred to peak heights as the latter are more dependent on the operating conditions. In this way, graphs of peak area against μmoles injected were constructed for oxygen and carbon monoxide.

A similar method was used for all other compounds. Suitable pressures of each compound were allowed into the known volume of the injection system U tube

at known temperatures, cooled in liquid nitrogen, and injected on to the appropriate column by warming to 70°C. Graphs of peak area against pressure of compound in injection system at 20°C were obtained.

Calibration of flame ionisation detector.

As the flame ionisation detector was about 50 times more sensitive than the katharometer, very small pressures of compounds were necessary for calibration. This was achieved by measuring accurately on the pressure transducer the pressure, ~1 cm, in the mixing vessel of the compound to be calibrated and making the total pressure of the mixture up to about 60 cm with isobutane. Small pressures of the resultant mixture were used for calibration as in the previous paragraph. Only isobutene, isobutene oxide and acetone were calibrated in this way. Calibration factors for all other compounds were calculated from relative values given by Sternberg [76].

Table 3

Calibration Factors. 1 p.u. = 1 Planimeter unit = 0.001 Sq. in.

Compound	Katharometer Response	Flame Ionisation Detector Response.
Oxygen	35.12 p.u. / μmole	-
Carbon Monoxide	385.0 " "	-
Ethylene	74.3 p.u. /mm Hg in U tube	2033 p.u. / mm Hg in 1.8ml at 20°C
Carbon Dioxide	75.4 " " " "	-
Propylene	94.0 " " " "	3050 " " " "
Isobutane	113.0 " " " "	-
Isobutene	105.4 " " " "	4244 " " " "
Acetaldehyde	67.8 " " " "	1529 " " " "
Propylene Oxide	83.4 " " " "	2157 " " " "
Isobutene Oxide	110.8 " " " "	2876 " " " "
Propionaldehyde	75.5 " " " "	2294 " " " "
Isobutylaldehyde	94.8 " " " "	3058 " " " "
Acetone	85.0 " " " "	2226 " " " "
Methacrolein	89.8 " " " "	3058 " " " "
Methanol	55.3 " " " "	832 " " " "
Water.	217.4 p.u. / μ mole	

Colorimetric Methods.

Formaldehyde was determined by a variation of the method of Bricker and Johnson [77]. Chromotropic acid reagent was prepared by dissolving 2 gm of chromotropic acid in 200 ml H_2O and 800 ml 25N H_2SO_4. The formaldehyde sample was cooled in liquid nitrogen in the detachable trap, detached and while still cooled in liquid nitrogen chromotropic acid reagent was added to the bulb which was then immersed in a suitable volume of reagent in a test tube. After the solution had been heated for 30 minutes in a boiling water bath with frequent shaking, it was transferred to a 20 ml graduated flask and, on cooling, was made up accurately to the mark. 10 ml of the coloured solution were added to 1 ml of water and 2 ml of thiourea (46% w/w) and the absorption of the coloured solution was compared to that of a blank determination using 10 mm silica cells in an S.P. 600 Spectrophotometer at a wavelength of 5700 $\overset{o}{A}$. The concentration of the original formaldehyde solution could then be obtained from a previously constructed calibration graph.

Hydrogen Peroxide was determined by the method of Egerton et al.[78] 200 ml of conc H_2SO_4 were added to 20 ml stock solution of $TiSO_4$, the solution made up to 1000 ml with water and dilute hydrogen peroxide added until the solution was pale yellow in colour. 1 ml of this solution was added to 3 ml of an aqueous solution of the reaction products and the absorbance of the yellow solution determined using 10 mm silica cells in an S.P. 600 spectrophotometer at a wavelength of 4100 $\overset{o}{A}$. The concentration of the hydrogen peroxide in the original solution was then determined from a previously constructed calibration graph.

3. Run Procedure.

3.1 Pumping Procedure.

A standard pumping procedure was employed as the reaction rate was sensitive to the condition of the reaction vessel walls. Reaction products were left in the reaction vessel overnight and at other times when no oxidations were being

carried out. After these products had been pumped off and the pressure reduced to 10^{-4} - 10^{-5} mm Hg, the reaction vessel was pumped out for thirty minutes.

3.2 Kinetic Procedure.

The mixing vessel was evacuated and the reactants introduced in the order - isobutane, oxygen - by means of a "piling up" process. After the reaction vessel and pressure transducer had been evacuated, they were connected to the mixing vessel and the required pressure of mixture allowed to enter the reaction vessel. Thirty seconds were allowed for the equilibration of the reactants and the tap between the reaction vessel and the mixing vessel and mercury manometer was closed. The initial pressure of the mixture could then be read on the manometer. Pressure increase in the system was followed by the increase in the output of the differential pressure transducer.

3.3. Analytical Procedure.

a) for oxidations using katharometer detection.

Samples for analysis were obtained by allowing the reaction mixture to come to equilibrium for thirty seconds with a previously evacuated sample bulb which was maintained at room temperature by a surrounding Dewar flask containing water at room temperature. The pressure increase prior to sampling and the pressure decrease due to sampling were obtained from the recorder trace of the transducer output. After thirty seconds, the reaction vessel tap and the sample tube tap were shut and the sample manifold was re-evacuated, a process requiring three minutes. A maximum of ten samples could be taken by repeating this process and the recorder trace gave a complete picture of the pressure changes caused by the increase in extent of reaction and the removal of samples. By this method, reproducibility was greater than could be obtained by carrying out ten separate runs and taking one sample from each at varying pressure increases.

As trial experiments had shown that many of the oxygenated compounds had appreciable vapour pressures at - 80°C and that a clean separation of hydrocarbons and oxygenated compounds could not be achieved by cooling samples to this temperature, two experiments were carried out under identical conditions but the sets of samples taken were analysed for different products.

1) for O_2, CO, C_2H_4, CO_2, C_3H_8, C_3H_6, i C_4H_{10} i C_4H_8, H_2O

The sample bulbs were cooled to - 193°C and the non-condensable gases, from each sample bulb in turn, transferred to the gas burette by means of a Toepler Pump in which the number of moles in the fraction was measured. An aliquot of this fraction was then admitted to the gas chromatography injection system and subsequently analysed on column 1. Oxygen, nitrogen, methane and carbon monoxide were eluted in that order.

The sample bulbs were warmed to - 80°C and products non-condensable at this temperature distilled from a sample bulb to the U tube of the injection system which was cooled to - 193°C in liquid nitrogen. Samples were injected by warming the U tube to 60°C with water and analysis carried out on column 2. The process was repeated until the contents of all the sample bulbs had been analysed. The "hydrocarbon fraction" was eluted in the order ethylene, carbon dioxide, propane, propylene, isobutane, n-butane and isobutene.

Water was then distilled from the sample bulb at ~ 70°C to the chromatography U tube at - 193°C, injected as above and analysed on column 5.

2). for oxygenated compounds.

Gases, non condensable at - 193°C, were pumped off. Oxygenated compounds were distilled to the chromatography U tube by warming the sample bulbs to 60°C. Analysis was carried out on column 3. Oxygenated compounds were eluted in the order acetaldehyde, propylene oxide, isobutene oxide, propionaldehyde, acetone, methacrolein and methanol.

The identities of all the products were checked by comparing the retention times of standard samples and reaction product mixtures on various gas-liquid chromatography columns.

b) For Initial Stage Runs using Flame Ionisation Detection.

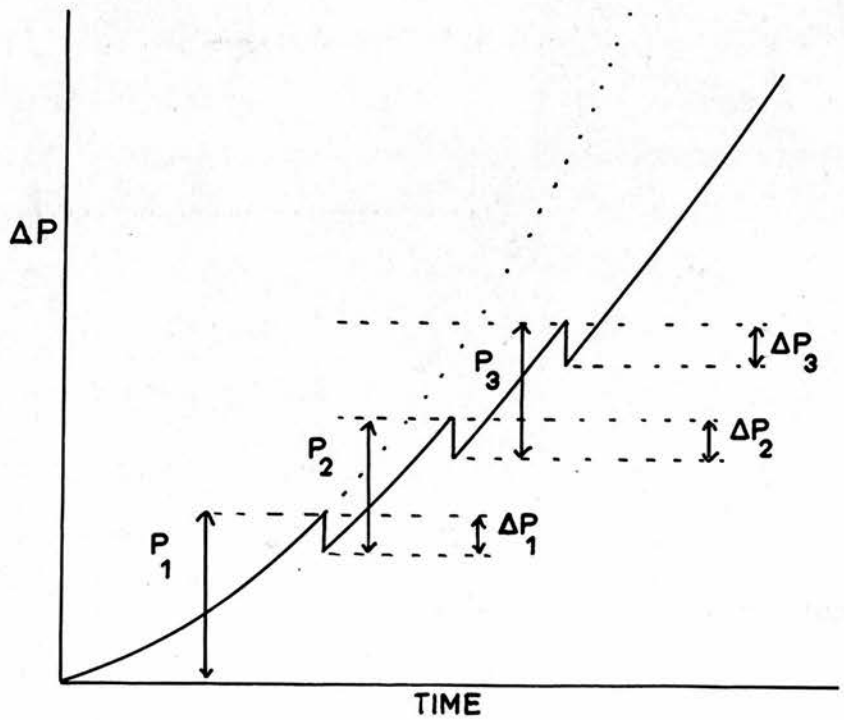
During the initial stage experiments, the pressure increase could not be measured accurately and time was not a reliable measure for the extent of reaction. Correlation between different runs could not be made by means of the pressure increase or time of reaction. Thus, samples taken at the same pressure increase were analysed for both oxygenated compounds and hydrocarbons and the extent of reaction was determined by the total number of mm atoms of Carbon in the products. The sampling method used in a) was modified so that on sampling two sample bulbs were filled with reaction products. Gases, non-condensable at - 193°C, were pumped off and discarded. Samples were distilled to the injection system as in a) 2. Products from one sample bulb were analysed for hydrocarbons using column 7 and products from the second of the pair of sample bulbs were analysed for oxygenated compounds on column 6. Before each set of analyses, the flow rates of air, carrier gas and the additional hydrogen stream were checked.

c) Formaldehyde and Hydrogen Peroxide.

The sampling procedure was carried out as in 3.3a) above but only three samples were taken for formaldehyde determinations and only one was taken for hydrogen peroxide determination.

4. Calculation of Results.

The method of sampling was such that the pressure of each product in the reaction vessel after sampling is equal to the pressure in the sample bulb. The pressure increase before sampling and the pressure decrease due to sampling were known from the appropriate changes in transducer output. To calculate the actual pressure of any product in the reaction vessel, it was necessary to multiply the pressure found in the sample bulb by a factor which allowed for the decrease of pressure on sampling. In the case of the first sample, the factor was equal to the ratio of the reaction vessel pressure before sampling to the reaction vessel pressure after sampling. Similar corrections had to be made for successive samples. Both the product pressures and the pressure rises required correction as the pressure increase at any given time was lower than that which would have been obtained (theoretical pressure increase) had no samples been removed. This method of calculation is most easily described with the aid of a diagram.



ΔP_1, ΔP_2 etc. are the pressure decreases due to removal of samples 1, 2 ..... etc.

and P_1, P_2, P_3 ..... are the actual pressure increases from start of reaction to sample 1, from sample 1 to sample 2, from sample 2 to sample 3 ..... etc.

Then, if P_o is the initial pressure in the reaction vessel.

Reaction vessel pressure before removal of sample 1 $= P_o+P_1$

(Theoretical final pressure)

Pressure decrease due to sampling $= \Delta P_1$

Actual pressure after sampling $= P_o+P_1 - \Delta P_1$

$\therefore$ Correction factor $= \dfrac{P_o+P_1}{P_o+P_1 - \Delta P_1} = C_1$

Theoretical pressure rise $= P_1$

Sample 2

Actual Pressure increase $= P_2$

Corrected Pressure increase $= P_2C_1$

Theoretical final pressure $= P_o+P_1+P_2C_1$

Theoretical pressure rise (from start of reaction) $= P_1+P_2C_1$

Actual pressure before sampling $= P_o+P_1 - \Delta P_1+P_2$

Actual pressure after sampling $= P_o+P_1 -\Delta P_1+P_2 - \Delta P_2$

$\therefore$ Corredtion factor $= \dfrac{P_o+P_1+P_2C_1}{P_o+P_1 - \Delta P_1+P_2 - \Delta P_2} = C_2$

This process of calculation was repeated for successive samples.

Product Pressures

The pressures of oxygen and carbon monoxide for a particular theoretical pressure rise ΔP_n where n is the sample number, are given by the equation

$$P(\text{mm Hg}) = \frac{\text{Peak Area}}{\text{Calib. Fact.}} \times \frac{\text{F.R.}}{\text{C.F.R.}} \times \frac{\mu \text{ total}}{\mu \text{injected}} \times \frac{22400 \times 760 \times T}{273 \times V_n} \times C_n$$

where Peak Area is given in planimeter units.

Calibration Factor is in planimeter units /μmole.

F.R. is carrier gas flow rate measured after sample analysis.

C.F.R. is calibration flow rate = 25 ml/min.

T = sampling temperature $^{\circ}K$.

V_n = volume of sample bulb, n.

C_n = correction factor for removal of n samples.

μtotal = total no. of moles in sample.

μinjected = no. of moles injected.

The above equation with μtotal = μinjected is used for the calculation of water pressures.

Hydrocarbon and oxygenated compound pressures are given by the equation.

$$P\ (\text{mm Hg}) = \frac{\text{Peak Area}}{\text{Calib. Fact.}} \times \frac{\text{F.R.}}{\text{C.F.R.}} \times \frac{3.010}{V} \times \frac{T}{293} \times C_n$$

where the peak area is in planimeter units.

Calibration factor is in planimeter units /mm Hg pressure in 3.010 ml.

F.R. is the observed flow rate of carrier gas.

where C.F.R. is the calibration flow rate = 25 ml/min for hydrocarbons.

= 30 ml/min for oxygenated compounds.

T = sampling temperature ^{o}K.

V = volume of sample bulb.

C_n = correction factor for the removal of n samples.

In the case of formaldehyde, product pressure is given by

$$P\ (mm\ Hg)\ CH_2O = \frac{\text{Absorbance}}{\text{Calibration factor}} \times V \times \frac{C_n}{V_B} \times G$$

where the calibration factor is given in absorbance units /µg /ml

V = vol. of solution of formaldehyde

C_n = correction factor for samples removed

V_B = volume of sample bulb

G = a factor converting a weight of formaldehyde to a pressure in a bulb of volume 4 ml at $20^{o}C$.

Hydrogen peroxide pressures are given by the formula:

$$P\ (mm\ Hg) = \frac{\text{Absorbance}}{\text{Calib. factor}} \times \frac{\mu\text{moles in RV.}}{\mu\text{moles in sample}} \times V \times \frac{760 \times T_R \times 22400}{V_R \times 273}$$

where the calibration factor is in absorbance units /µg/ ml.

V = the volume of solution

T_R = reaction vessel temperature

V_R = reaction vessel volume

5. Preparation and Purification of Materials.

1. Column Packings

a) Partition Chromatography

The required amount of stationary phase (polyethylene glycol, dinonyl phthlate, acetonyl acetone or dibutyl phthlate) was dissolved in a suitable solvent and added with mixing to the inert support (celite or fosalsil). The solvent was drawn off at the water pump and the dry inert support plus stationary phase packed in 5 ft. lengths of 4 mm i.d. Pyrex tubing.

b) Adsorption Chromatography

Pellets of Linde Molecular Sieve (13X) were crushed and sieved. A sample of mesh (60-80) was roasted in a crucible over a Meker burner for seven hours. The molecular sieve was cooled in a desiccator and packed in a 3 ft. glass 4 mm i.d. column.

2. Reactants.

Isobutane (British Petroleum Co. Ltd.) was taken from a cylinder and collected at - 193°C. Repeated distillations from - 80°C to - 193°C were carried out in the apparatus, the middle fraction being retained in each case. Analysis by gas chromatography showed that the impurities were n-Butane 0.4% and Propane 0.04%.

Isobutene (British Petroleum Co. Ltd.) was treated in a similar way, the only impurities being 0.1% propylene and 0.3% isobutane.

Propane (I.C.I. Ltd. Heavy Organic Chemicals Division) contained 0.2% ethane, 0.3% propylene and 1.6% isobutane.

Oxygen and Nitrogen were drawn from B.O.G. cylinders, passed through liquid nitrogen traps to remove any condensable impurities and allowed to leak into five-litre bulbs.

The gases used for the calibrations, apart from those mentioned above, were obtained as follows:-

Carbon monoxide was prepared by dropping formic acid on to concentrated sulphuric acid heated to 100°C in vacuum. The carbon monoxide evolved was purified by passage through two traps at - 183°C and stored in the apparatus.

Ethylene was taken from a B.O.G. cylinder and not purified further.

Propylene was prepared by dehydrating isopropanol with phosphorous pentoxide. After passage through at trap at - 80°C, the propylene was collected at - 193°C. No impurities could be detected by gas chromatographic analysis.

Carbon Dioxide was commercial "Drikold" which was purified by vacuum distillation, the middle fraction being retained.

Acetaldehyde, Propionaldehyde, Isobutyraldehyde and Methacrolein were B.D.H. reagents. Each aldehyde was distilled, the middle fraction retained and a few crystals of hydroquinone added to each sample to prevent polymerisation.

Propylene Oxide B.D.H. Laboratory Reagent.

Isobutene Oxide was a gift sample from I.C.I. (H.O.C. Division) and contained about 2% of each of acetone and diethyl ether. The impurities were removed by preparative scale gas chromatography.

Acetone - Analar Acetone.

Methanol - Absolute Methanol.

3. Preparation of Reaction Vessel Surfaces.

a) Boric Acid coating

A saturated solution of boric acid in water was allowed to stand in the reaction vessel overnight. The solution was removed and the reaction vessel allowed to drain in a vertical position for thirty minutes before being fused to the apparatus.

b) Hydrogen Fluoride washed

The reaction vessel was washed with hot water to remove any traces of alkali coating and then rinsed with a 40% solution of hydrogen fluoride. The reaction vessel was again allowed to drain for thirty minutes before being sealed to the apparatus.

c) Potassium Chloride coating

A 10% solution of potassium chloride was allowed to remain in the reaction vessel for thirty minutes and allowed to drain as in a) and b) above.

d) Silver Coating

A coating of silver was deposited on the walls of the reaction vessel by the action of a mixture of reducing sugars on ammoniacal silver nitrate. The vessel was thoroughly washed with distilled water before being sealed on to the apparatus.

3. Experimental Results.

1) The Overall Reaction.

In this section, the results are presented of experiments in which the formation of products and consumption of reactants have been followed over the complete pressure rise. The reactions were followed until all the oxygen initially present had been used up. Experiments were carried out in a "conditioned" reaction vessel and analysis throughout was by gas chromatography using katharometer detection. The effect of hydrocarbon:oxygen ratio on product distribution at 300°C was studied by keeping the initial mixture pressure constant at 200 mm and varying the isobutane: oxygen ratio by a factor of 18. Temperature dependence of product distribution has been studied by carrying out oxidations of 2:1 isobutane: oxygen mixtures at 270°C and 330°C and comparing the results of these experiments to those obtained for a 2:1 isobutane: oxygen mixture at 300°C. Table 4 lists the experimental conditions used for these studies. Results for each individual set of conditions are given in the tables and figures whose numbers are listed in the right hand columns of Table 4.

Table 4:

Run Nos.	Temp. °C	Initial Pressure (mm)	iC_4H_{10} (mm)	Oxygen (mm)	Isobutane / Oxygen	Table No.	Figure No.
2,3,	300	200	100	100	1.0	5	5
6,7,	300	200	133	67	2.0	6	6
8,9,	300	200	67	133	0.5	7	7
10,11,12	300	200	160	40	4.0	8	8
13,14	300	200	180	20	9.0	9	9
16,17	270	260	170	90	2.0	10	10
18,19,20	330	100	67	33	2.0	11	11
24,25	270	400	267	133	2.0	12	12

Although no precise kinetic data was collected, the general kinetic features of the oxidations are of interest. All reactions showed the characteristics of a degenerate branching chain reaction, an induction period of negligible reaction being followed by a period of slow acceleration to the maximum rate after which the rate of pressure increase fell off at a rate which was dependent on the isobutane: oxygen ratio. In oxygen weak mixtures, the rate of reaction fell to zero soon after the maximum rate of reaction had occurred while in oxygen rich mixtures the decrease in reaction rate was much more gradual. The length of the induction period decreased with increase in temperature and increase in hydrocarbon: oxygen ratio and the maximum rate of reaction increased with temperature and initial pressure of mixture. For example, for a 1:2 isobutane: oxygen mixture at 300°C and 200 mm the induction period was 50 minutes and the complete reaction lasted three hours while 4:1 and 9:1 isobutane: oxygen mixtures at the same initial temperature and pressure had induction periods of one minute and the complete reactions lasted thirty minutes. Although the oxidation of a 2:1 mixture of isobutane:oxygen at 200 mm and 300°C took about forty-five minutes to reach completion, an identical mixture at 330°C had reacted fully in three minutes. When the pressure of the 2:1 isobutane:oxygen mixture at 330°C was reduced to 100 mm, the reaction had an induction period of 5 minutes and took 40 minutes to reach completion. Despite the considerable amount of "ageing" the reaction vessel had undergone before use, the rates of reaction under identical experimental conditions were not completely reproducible.

The general analytical features are similar in all oxidations, the relative yields of products being little affected by reaction temperature or variation in mixture composition. Isobutene is, in all cases, the major initial product and accounts for 70-80% of the isobutane consumed in the initial stages. Water is also a major product. The pressure of carbon monoxide is initially less than that of carbon dioxide but, in every case, as the reaction proceeds, the formation of carbon monoxide increases until its pressure exceeds that of carbon dioxide. From figures 5-9 it is clear that, as the extent of reaction increases, the isobutene /ΔPplot is curving towards the ΔPaxis and that in one case of an oxygen rich mixture, (Figure 7), the isobutene yield goes through a maximum. At such extents of reaction, isobutene is undergoing oxidation and the general picture of the oxidation is complicated by the oxidation of the products. The isobutane pressure at the maximum in the isobutene yield is 8 times that of the isobutene. Since isobutene is being removed as quickly as the isobutane, the radical mixture must attack isobutene about 8 times as fast as it attacks isobutane. The minor products detected were (in order of decreasing abundance) acetone, propylene, carbon dioxide, isobutene oxide, propionaldehyde, acetaldehyde, carbon monoxide, methanol, propylene oxide, ethylene, methacrolein and methane. The relative yields of the minor products are independent of the hydrocarbon: oxygen ratio which was varied by a factor of 18 in these experiments. Near the maximum rate of reaction, the yields of propionaldehyde and possibly acetaldehyde are observed to pass through maxima indicating that their rate of consumption exceeds their rate of formation. After this series of runs had been carried out, discovery was made that isobutyraldehyde could not in fact be separated from acetone on the chromatography column used. Acetone pressures given in tables 5-12 thus include some isobutyraldehyde but, as acetone is

certainly present in much greater yields than isobutyraldehyde, any error in the acetone pressure should not be large. Ethane and ethylene were known to be inseparable on the chromatography column used but, as preliminary work using other columns had shown that ethane formed was about 5% of the ethylene formed, the C_2 product was taken as ethylene. Towards the end of the reaction, the major products are the oxides of carbon, water, acetone and isobutene. An increase in the yields of methanol and methane is also detected. Methane is observed only when the oxygen present in the reaction mixture is almost exhausted. Methyl and methoxy radicals must be present in the system and, although these radicals usually undergo oxidation, H abstraction to form methane and methanol may occur when the oxygen concentration is low.

The results from these runs have been plotted as pressures of products (or reactants) against pressure rise. An ideal measure of the extent of reaction would have been the consumption of one of the reactants but neither of these consumptions can be measured with accuracy as both involve the subtraction of two large quantities. That the pressure rise is a reliable measure of the extent of reaction is shown in figure 13, in which the oxygen consumptions for mixtures of varying hydrocarbon:oxygen ratios are plotted against the pressure rises in the reaction vessel. For all mixtures the oxygen consumption is proportional to the pressure rise, the proportionality factors ranging from 2 to 3.

As described in the section on experimental technique, separate runs, under identical experimental conditions, were carried out for determination of the yields of the hydrocarbon fraction and of the oxygenated compound fraction. The product pressures were correlated by means of the pressure rise and a composite picture of each reaction shown in figures 5-12. However, the effects of mixture composition and temperature on the relative

yields of products are best illustrated by plotting the number of mm atoms of carbon per individual product against the number of mm atoms of carbon in the total product. The values of total mm atoms of carbon have to be calculated from the product pressure against ΔP curves (figures 5-12) as experimental points in different runs rarely occur at identical pressure rises. The number of mm atoms of carbon in the total product is found by multiplying the pressures of each product at a given pressure rise by the number of carbon atoms in that product and summing for all products. This total number of mm atoms carbon is equal to four times the number of mm of isobutane consumed. The initial gradients of the lines in figures 15-22 represent the fractions of the isobutane consumed which are converted to individual products. In figure 16, the initial fractional yield of acetone is given as 0.065. This means that of every 100 carbon atoms (25 mm isobutane) consumed in the reaction, 6.5 will be found in acetone the pressure of which will be 2.2 mm. Plots of oxygen consumption against mm atoms C in total product (figure 14) show that the oxygen consumption is proportional to the total mm atom C in the products. This result is expected as the extent of reaction which is proportional to the total mm atoms C in the products is also proportional to the pressure rise. However, the proportionality factor (figure 14) is not constant but decreases as the isobutane:oxygen ratio decreases. As the mm atom C of the total product is equal to four times the number of mm of isobutane consumed, the ratio of the consumption of oxygen to the consumption of isobutane is given by four times these proportionality factors. Thus, the ratio oxygen consumed:isobutane consumed falls from 2.2 to 1.3 as the isobutane:oxygen ratio increases from 0.5 to 9. To some extent this is explained by the greater proportion of minor oxygenated products which is formed in oxygen rich mixtures. More oxygen is consumed per molecule

of isobutane when the percentage of oxygenated compounds formed is high than when the percentage of olefins formed is high.

The effect of variation of mixture composition on initial yield of products are shown on Figures 15-22. No initial yield of any product varies by more than a factor of two although the oxygen pressure varies by a factor of seven. The most prominent features are:

1) the initial yield of isobutene increases with the isobutane:oxygen ratio.
2) the initial yield of acetone decreases with increase in isobutane:oxygen ratio.
3) the initial yields of carbon monoxide and carbon dioxide are greatest in mixtures of low isobutane:oxygen ratio.
4) the initial yields of acetaldehyde and propionaldehyde increase as the isobutane:oxygen ratio decreases.
5) No general trend is observed for isobutene oxide or propylene.
6) All products mentioned in 1)-5) above appear to be initial productsof isobutane oxidation.

The effects of temperature on the initial yields of products are shown on Figures 23-27. The initial yields of olefins, isobutene and propylene, increase with increase in temperature while the initial yields of acetone and the aldehydes decrease. The initial product yields which have been shown in Figures 15-27 are listed in Tables 13 and 14.

Initial product yields from oxidations at 270°C of 2:1 isobutane:oxygen mixtures at initial pressures of 260 mm and 400 mm showed no significant dependence on total pressure. No variation was found in the initial yields of isobutene, acetone, and carbon dioxide. Slight variations were found in the initial yields of other products. The yields of aldehydes increased with increase in pressure while those of carbon monoxide, propylene, isobutene

oxide and methanol decreased.

Activation energy differences between competing reactions were calculated by the method outlined in section 4 of the introduction to this thesis. Although oxidations were not carried out at a sufficient number of temperatures for detailed activation energy differences to be calculated, approximate values were obtained. The activation energy difference between the reactions forming isobutene and acetone was about 8 k cal while that between the reactions forming isobutene and propylene was 7 k cal.

Check experiments were carried out at 330°C to determine the effect of the multi-sample method employed in this work on the subsequent stages of the oxidation. 2:1 isobutane:oxygen mixtures were oxidised at 100 mm initial pressure and several sample bulbs filled at a suitable pressure rise. Analysis was carried out for all products. To minimise errors in analysis, the contents of two or more sample bulbs were analysed for the same group of products. The product pressures were then compared with those obtained in oxidations where six or seven samples had been removed before a similar pressure rise had been reached. No difference greater than experimental error was observed. Removal of samples from the reaction mixture does not then change the subsequent product distribution.

Product formation occurs in a manner parallel to the pressure increase i.e. exponentially with time. Figure 28 shows that both major and minor products are formed exponentially with time and that the branching factors for all products are constant.

The yields of formaldehyde have been determined for only two sets of experimental conditions, the results being shown in Tables 15 and 16. The formaldehyde/ΔP curves have been included in the appropriate figures

(Figures 6 and 11) which show that formaldehyde is an important initial product. The yield of formaldehyde is greater at 300°C than at 330°C but, unlike propionaldehyde and acetaldehyde yields, the yield of formaldehyde does not go through a maximum near the maximum rate of reaction.

Hydrogen peroxide determinations were carried out at 300°C using a 2:1 mixture of isobutane:oxygen at 200 mm initial pressure. Results were completely irreproducible. Hydrogen peroxide pressures found were of the order of 1 mm as shown in Table 17. This result indicates that hydrogen peroxide, if it is formed during the oxidations, must be decomposing on the walls of the reaction vessel.

Element Balances.

Element balances calculated from graphs of product pressure against pressure rise are given in Tables 5A-12A. Pressure balances are also given. Carbon balances are generally good although the accuracy of any particular balance is largely determined by the accuracy of the residual isobutane pressure. Hydrogen balances are slightly lower than carbon balances but are still reasonably good. Oxygen and pressure balances are generally low, the deficiences becoming greater with extent of reaction. Such deficiences suggested that the products which were not being measured contained only hydrogen and oxygen and, before hydrogen peroxide and formaldehyde determinations were carried out, these products were thought to be largely hydrogen peroxide. Further consideration of the results showed that if the experimental water pressures were disregarded and the oxygen deficit supposed to be due entirely to water pressure the total pressure could be balanced with an accuracy comparable to that of the carbon balance. The calculated water pressure given in the tables is equal to the mm atom deficit of Oxygen. Experimental values for the pressure of

water were considerably scattered due to the difficulty with which water is distilled throughout the analytical system. It is possible that these experimental values are low. That no carbon containing product has been omitted is shown by the consistency of the carbon balances.

Estimation of t-butyl hydroperoxide.

T-butyl hydroperoxide was relatively stable at 300°C and, although t-butanol and acetone were formed if mixtures of isobutane and t-butyl hydroperoxide were left in the reaction vessel for ten minutes, more than 50% of the original peroxide could be determined by gas chromatography. The retention times of t-butanol, acetone and t-butyl hydroperoxide were determined at 73°C on a 5 ft. column of 20% dinonyl phthalate on celite. Large samples of oxidation products of 9:1 and 2:1 isobutane:oxygen mixtures at 300°C were analysed but no hydroperoxide was detected. As complete decomposition of peroxide to t-butanol and acetone could have occurred, end product analysis was carried out for t-butanol. Only trace amounts were detected. This investigation showed that t-butyl hydroperoxide was not formed in detectable amounts in isobutane oxidation at 300°C.

Table 5 (Figure 5)

Ratio $iC_4H_{10}:O_2$ = 1:1 Pressure = 200 mm Hg Temp = 300°C

Pressure in reaction vessel (mm Hg)

ΔP mm Hg	O_2	iC_4H_{10}	C_2H_4	CO_2	C_3H_6	CO	iC_4H_8	H_2O
1.93	98.4	-	-	-	-	0.49	-	-
5.15	82.0	102.5	0.00	3.00	0.53	2.35	4.72	4.33
8.92	87.9	94.2	0.23	5.19	1.14	4.97	6.97	4.60
13.32	71.8	87.9	0.37	7.78	1.69	8.78	7.84	5.77
20.22	48.8	86.7	0.78	12.3	2.76	19.2	9.20	8.29
26.34	24.5	89.8	1.02	17.8	3.82	29.7	10.40	8.78
31.47	12.0	79.1	1.18	21.6	4.19	39.4	10.4	7.76
34.64	0.6	79.4	1.10	24.2	5.21	47.8	10.8	8.01

ΔP mm Hg	CH_3CHO	$CH_2\overset{O}{\diagdown}\overset{}{\diagup}CH\text{-}CH_2$	$(CH_3)_2\overset{O}{\diagdown}\overset{}{\diagup}C\text{-}CH_2$	C_2H_5CHO	CH_3COCH_3	CH_3OH
0.10	0.00	0.00	0.00	0.00	0.07	0.00
1.23	0.21	0.04	0.07	0.18	0.31	-
3.44	0.48	0.05	0.23	0.30	0.90	-
6.94	0.73	0.13	0.55	0.56	1.31	0.36
12.44	1.18	0.49	1.16	0.67	3.58	0.66
18.79	1.75	0.40	2.11	0.70	-	2.06
24.76	2.03	0.62	3.21	0.77	9.42	2.41
30.76	2.46	0.99	4.27	0.72	14.2	3.98
33.43	2.32	1.15	4.94	0.00	16.8	6.29
34.36	2.29	1.21	4.61	0.00	18.1	8.42

Table 6 (Figure 6)

Ratio $iC_4H_{10}:O_2$ = 2:1 Pressure = 200 mm Hg Temp = 300°C

Pressure in reaction vessel (mm Hg)

ΔP mm Hg	O_2	CO	C_2H_4	CO_2	C_3H_6	iC_4H_{10}	iC_4H_8	H_2O	CH_4
1.64	62.2	0.44	0.00	0.76	0.01	137.7	2.27	-	-
2.29	63.3	1.07	0.00	1.44	0.27	134.3	3.42	3.49	0.00
4.32	58.2	2.32	0.00	2.65	0.74	126.6	5.61	11.5	0.00
6.24	51.2	3.76	0.15	3.44	1.11	122.5	6.23	12.5	0.00
9.47	42.1	6.68	0.15	5.42	1.71	123.4	8.99	-	0.00
12.94	31.6	10.6	0.27	7.48	2.54	117.7	10.4	-	0.00
16.34	16.3	14.5	0.47	9.14	3.87	119.5	11.7	-	0.00
20.30	3.6	21.8	0.65	12.00	4.17	118.7	12.8	-	0.09
21.41	0.2	24.1	0.60	12.90	4.23	112.1	12.9	-	0.30

ΔP mm Hg	CH_3CHO	$CH_2{<}^{CH}_{CH_2}{>}O$	C_2H_5CHO	$(CH_3)_2{<}^{C}_{CH_2}{>}O$	CH_3CO-CH_3	CH_3OH	M.A.
0.48	0.00	0.00	0.00	0.00	0.30	0.00	0.00
1.10	0.28	0.00	0.00	0.00	0.45	0.00	0.00
2.04	0.37	0.00	0.00	0.00	0.54	0.00	0.00
3.71	0.30	0.06	0.18	0.15	0.90	0.00	0.00
5.49	0.44	0.09	0.34	0.27	1.38	0.00	0.00
7.59	0.55	0.18	0.37	0.48	1.76	0.73	0.00
9.81	0.75	0.19	0.44	0.76	2.71	0.86	0.00
13.32	1.01	0.31	0.63	1.27	4.48	1.26	0.00
24.4	1.54	0.77	0.27	1.57	10.50	3.19	0.42

Table 5A

Element Balances. T = 300°C Isobutane:oxygen = 1:1 Pressure = 200 mm

ΔP	mm atoms			Total RV Pressure	H_2O (calc.)	mm atoms	Pressure
mm.	C	H	O	(mm)	mm.	H(calc)	mm (calc)
0	400	1000	200	200	-	-	-
2	406.4	1006	192	195.3	8.0	1021	203.3
4	416.4	1020	185.7	196.4	14.3	1048	210.4
5	420.1	1025	182.8	195.9	17.2	1058	212.9
6	421.9	1024	180.0	194.8	20.0	1063	214.8
8	426.9	1026	168.3	190.2	31.7	1089	221.9
10	433.0	1030	168.1	191.5	31.9	1084	223.4

Table 6A

Element Balances. T = 300°C Isobutane:oxygen = 2:1 Pressure = 200 mm

ΔP	mm atoms			Total RV Pressure	H_2O (calc.)	mm atoms	Pressure
mm.	C	H	O	(mm)	mm	H(calc)	mm (calc)
0	520	1300	140	200	-	-	-
2	527	1306	131.1	197.2	8.9	1324	206.1
4	535	1314	120.4	194.7	19.6	1353	214.3
6	539	1313	114.0	191.6	26.0	1365	217.6
8	543	1312	106.7	189.1	33.3	1376	222.4
10	548	1310	99.7	186.6	40.3	1390	226.9
12	552	1310	91.5	183.8	48.5	1407	229.3

Note: the experimental water values are not included in either the oxygen balances or the pressure balances.

Table 7 (Figure 7)

Ratio $iC_4H_{10}:O_2$ = 1:2 Pressure = 200 mm Hg Temp = 300°C

Pressure in reaction vessel (mm Hg)

ΔP mm Hg	O_2	CO	C_2H_4	CO_2	C_3H_6	iC_4H_{10}	iC_4H_8	H_2O	CH_4
0.58	141.5	0.00	0.00	0.24	0.00	60.1	0.31	0.00	0.00
1.65	134.1	0.30	0.00	0.68	0.03	58.5	1.10	0.72	0.00
3.32	-	0.87	0.00	1.42	0.19	56.9	2.16	3.46	0.00
6.70	116.3	2.22	0.05	2.73	0.40	52.1	3.25	7.82	0.00
9.84	110.7	4.66	0.18	4.34	0.67	50.5	4.32	13.93	0.00
14.57	88.7	9.57	0.46	7.42	1.10	45.9	5.23	-	0.00
20.4	79.3	18.23	0.83	12.08	1.57	43.6	5.48	-	0.00
26.5	66.2	31.6	-	19.42	2.07	39.7	5.12	-	0.00
32.0	52.5	43.2	1.26	24.6	2.48	38.4	5.07	-	0.02
38.9	36.5	60.6	1.37	29.8	3.04	33.5	4.81	-	0.07

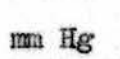
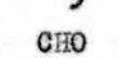
ΔP mm Hg	CH_3CHO			C_2H_5CHO	CH_3COCH_3	CH_3OH
0.83	0.15	0.00	0.03	0.09	0.17	0.00
1.86	0.32	0.00	0.09	0.26	0.47	0.00
3.27	0.40	0.05	0.19	0.35	0.78	0.36
5.99	0.68	0.08	0.44	0.54	1.57	-
9.02	0.90	0.14	0.84	0.75	2.79	0.71
13.32	1.18	0.20	1.27	0.75	4.29	0.88
17.26	1.43	0.38	1.84	0.78	6.47	1.72
21.85	1.40	0.50	2.18	0.86	8.15	2.44
26.81	1.66	0.73	2.86	0.82	10.77	3.41
31.78	1.55	0.85	2.94	0.65	13.31	4.59

Table 8 (Figure 8)

Ratio $iC_4H_{10}:O_2$ = 4:1 Pressure = 200 mm Hg Temp = 300°C

Pressure in Reaction Vessel (mm Hg)

ΔP mm Hg	O_2	CO	iC_4H_{10}	C_2H_4	CO_2	C_3H_6	iC_4H_8	H_2O
0.60	-	-	-	0.00	0.18	0.00	0.36	2.36
0.90	34.5	0.07	158.3	0.00	0.13	0.40	0.44	3.04
2.13	30.2	0.35	156.3	0.00	0.39	0.11	1.61	-
2.93	29.9	0.33	156.7	0.00	0.58	0.27	2.43	6.11
6.08	22.8	0.90	157.0	0.35	1.30	0.74	5.06	7.15
6.33	25.9	-	153.9	0.03	1.27	0.84	5.26	-
10.79	15.9	2.75	-	-	-	-	-	12.41
12.46	9.5	2.87	153.1	0.11	2.60	2.03	8.88	14.67
18.22	0.0	8.55	148.4	0.20	3.68	3.18	10.87	16.88
18.71	0.1	7.13	150.0	-	-	3.10	11.71	16.14

ΔP mm Hg	O_2	CO	CH_3CHO	$CH_2(CH)CH_2$	$(CH_3)_2C(O)CH_2$	C_2H_5CHO	CH_3COCH_3	CH_3OH	M.A.
0.77	34.5	0.00	0.05	0.00	0.04	0.01	0.11	0.00	0.00
1.80	34.2	0.23	0.09	0.00	0.06	0.05	0.18	0.00	0.00
3.26	30.4	0.48	0.24	0.00	0.18	0.19	0.42	0.00	0.00
5.64	27.9	1.20	0.46	0.06	0.46	0.35	0.98	0.41	0.00
9.01	18.4	2.48	0.92	0.10	1.03	0.43	2.11	0.69	0.00
13.13	11.3	4.40	1.34	0.20	1.63	0.39	3.44	1.76	0.09
18.32	0.0	7.22	-	-	-	-	-	-	-

Table 7A

Element Balances Temp = 300°C Isobutane:oxygen = 1:2 Pressure = 200 mm

ΔP	mm atom			Total R.V. Pressure	H_2O(calc)	mm atoms	Pressure
mm	C	H	O	(mm)	mm	H (calc)	mm(calc)
0	248	620	276	200	-	-	-
2	244	602	264.6	193.0	11.4	625	204.4
4	241	587	257	188.3	18.7	624	207.0
5	240	583	254	186.4	22.1	627	208.5
6	239	574	251	184.3	25.2	624	209.5
8	239	567	241	181.1	34.7	636	215.8
10	243	566	240	179.8	36.1	638	215.9

Table 8A

Element Balances Temp = 300°C Isobutane:oxygen = 4:1 Pressure = 200 mm

ΔP	mm atoms			Total R.V. Pressure	H_2O(calc)	mm atoms	Pressure
mm	C	H	O	(mm)	mm	H(calc)	mm(calc)
0	647	1618	76.4	200	-	-	-
2	640	1593	70.4	195.0	6.0	1605	201.0
4	642	1592	63.9	192.2	12.6	1617	204.8
5	645	1596	61.1	191.5	15.3	1627	206.8
6	647	1598	58.5	190.7	17.9	1633	208.6
8	654	1608	53.1	189.7	23.3	1654	213.0
10	664	1625	48.2	189.6	28.2	1681	217.8

Note: Experimental water values are not included in the oxygen and total pressure balances.

Table 9 (Figure 9)

$iC_4H_{10}:O_2$ ratio = 9:1 Pressure = 200 mm Hg. Temp = 300°C

Pressure in Reaction Vessel (mm Hg.)

ΔP mm Hg	O_2	CO	C_2H_4	CO_2	C_3H_6	iC_4H_{10}	iC_4H_8	H_2O
1.14	17.23	0.05	0.00	0.27	0.08	177.5	0.88	1.80
1.57	15.86	0.10	0.00	0.32	0.09	176.4	1.35	1.97
2.04	16.13	0.20	0.00	0.45	0.16	176.9	1.86	2.90
3.05	14.70	0.34	0.00	0.59	0.33	170.2	2.96	3.43
3.79	13.54	0.49	-	-	-	-	-	5.18
5.02	11.12	0.81	0.03	0.97	0.69	169.3	4.94	5.51
7.14	7.06	1.30	0.06	1.41	1.12	163.8	7.20	7.57
9.43	2.99	2.33	-	1.69	1.69	163.3	8.35	10.60
11.13	0.00	2.38	-	1.60	2.02	157.0	9.04	-

ΔP mm Hg	CH_3CHO	$CH_2\text{-}CH\text{-}CH_2$ (O)	C_2H_5CHO	$(CH_3)_2C\text{-}CH_2$ (O)	CH_3COCH_3	CH_3OH
0.99	0.00	0.00	0.00	0.00	0.09	0.00
1.74	0.08	0.00	0.04	0.05	0.19	0.00
2.46	0.11	0.00	0.08	0.11	0.34	0.00
3.31	0.19	0.00	0.15	0.20	0.52	0.00
4.37	0.26	0.03	0.16	0.32	0.71	0.00
5.82	0.38	0.07	0.20	0.50	1.04	0.40
7.03	0.50	0.10	0.26	0.74	1.52	0.90
8.42	0.65	0.12	0.21	0.93	1.84	0.94
10.00	0.82	0.15	0.19	1.20	2.40	0.99

Table 10 (Figure 10)

iC_4H_{10}:O_2 ratio = 2:1 Pressure = 260 mm Temp = 270°C

Pressure in Reaction Vessel (mm Hg)

ΔP mm Hg	O_2	iC_4H_{10}	CO	C_2H_4	CO_2	C_3H_6	iC_4H_8	CH_4	H_2O
0.91	86.4	168.3	0.10	0.00	0.39	0.05	1.22	0.00	0.32
1.71	84.2	167.4	0.25	0.00	0.65	0.11	1.94	0.00	1.95
4.03	78.1	164.7	0.75	0.01	1.64	0.36	4.16	0.00	5.09
6.62	72.0	158.0	1.71	0.04	2.58	0.65	5.69	0.00	9.54
10.00	61.2	159.5	3.61	0.09	3.94	1.02	7.57	0.01	11.83
16.3	38.2	158.3	9.22	0.13	6.71	1.77	9.91	0.03	16.50
21.18	-	156.9	13.09	0.23	9.37	2.29	10.95	-	18.19
28.16	2.80	157.4	27.41	0.25	12.06	-	11.69	0.24	-
31.07	0.18	-	28.00	-	-	-	-	1.01	-

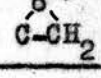
ΔP mm Hg	CH_3CHO		C_2H_5CHO		CH_3COCH_3	CH_3OH
0.73	0.10	0.00	0.25	0.09	0.28	0.00
1.71	0.21	0.00	0.43	0.17	0.58	0.00
2.83	0.34	0.05	0.48	0.30	0.99	0.35
5.81	0.69	0.07	0.73	0.69	2.28	0.81
9.62	1.30	0.13	0.91	1.22	4.43	1.50
13.38	2.24	0.21	0.91	1.79	7.24	2.90
17.21	2.94	0.28	0.92	2.53	9.84	4.28
21.91	3.66	0.44	0.72	2.88	12.84	5.33
27.37	3.69	0.63	0.54	3.85	17.80	9.81

Table 9A

Element Balances Temp = 300°C Isobutane:oxygen = 9:1 Pressure = 200 mm

ΔP	mm atoms			Total R.V.	H_2O(calc)	mm atoms	Pressure
mm	C	H	O	Pressure(mm)	mm	H(calc)	mm(calc)
0	716	1790	42	200	-	-	-
2	706	1759	35.2	193.9	6.8	1772	200.7
4	702	1742	29.8	190.1	12.2	1766	202.3
5	700	1734	28.1	188.4	13.9	1761	202.1
6	700	1729	24.8	186.9	17.2	1763	204.1
8	702	1728	20.1	185.1	22.0	1772	207.1
10	703	1728	15.5	183.4	26.5	1781	209.9

Table 10A

Element Balances Temp = 270°C Isobutane:oxygen = 2:1 Pressure = 260 mm

ΔP	mm atoms			Total R.V.	H_2O(calc)	mm atoms	Pressure
mm	C	H	O	Pressure(mm)	mm	H(calc)	mm (calc)
0	678	1696	176.8	258.	-	-	-
2	684	1700	168.5	254.8	8.3	1717	263.1
4	691	1708	160.3	252.1	16.5	1739	268.5
5	695	1710	152.5	248.9	24.3	1759	273.2
6	701	1717	145.2	246.7	31.6	1780	278.3
8	692	1708	156.8	250.5	20.0	1748	270.5
10	708	1723	138.5	244.7	38.3	1800	283.0

Note: Experimental water values are not included in either the oxygen or pressure balances.

Table 11 (Figure 11)

iC_4H_{10}:O_2 ratio = 2:1 Pressure = 98 mm Temp = 330°C

Pressure in Reaction Vessel (mm Hg)

ΔP mm Hg	CO_2	C_3H_6	iC_4H_{10}	iC_4H_8	H_2O	ΔP mm Hg	O_2	CO	CH_4
0.14	0.16	0.03	63.0	0.44	1.66	0.18	33.6	0.09	0.00
0.45	0.18	0.06	61.2	0.91	1.37	0.81	32.1	0.21	0.00
1.20	0.41	0.18	60.1	1.77	3.14	2.13	27.6	0.68	0.00
2.15	0.63	0.35	58.2	2.50	4.62	3.85	24.9	1.39	0.00
3.56	0.91	0.61	57.4	3.60	9.05	5.97	21.1	2.49	0.02
5.31	1.38	0.95	52.8	4.50	12.26	8.21	-	3.42	-
7.09	1.70	1.35	51.7	5.25	12.96	10.73	10.8	5.78	0.05
9.35	2.16	1.78	48.4	5.68	15.92	12.73	6.4	6.99	0.08
12.61	3.14	2.46	46.9	6.74	21.18	16.09	0.55	11.60	0.21

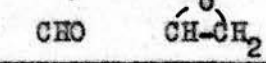
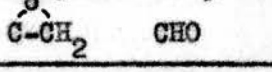
ΔP mm Hg	CH_3CHO			C_2H_5CHO	CH_3COCH_3	M.A.	CH_3OH
0.32	0.03	0.00	0.00	0.00	0.06	0.00	0.00
1.36	0.09	0.00	0.00	0.00	0.13	0.00	0.00
2.17	0.16	0.00	0.08	0.12	0.38	0.00	0.00
3.01	0.27	0.00	0.11	0.13	0.48	0.00	0.00
3.98	-	-	-	-	0.81	0.00	0.00
5.32	0.37	0.07	0.31	0.26	1.16	0.00	0.00
6.98	0.48	0.12	0.36	0.18	1.58	0.00	0.00
9.86	0.52	0.17	0.53	0.21	2.33	0.18	0.34
12.05	0.59	0.25	0.59	0.17	3.07	0.20	0.50

Table 12 (Figure 12)

iC_4H_{10}:O_2 ratio = 2:1 Pressure = 400 mm Hg Temp = 270°C

Pressure in Reaction Vessel (mm Hg)

ΔP mm Hg	O_2	CO	CO_2	C_3H_6	iC_4H_{10}	iC_4H_8	H_2O
0.36	127.7	0.09	0.15	0.00	271.3	0.21	0.81
0.86	128.2	0.09	0.24	0.02	273.7	0.69	0.98
1.70	125.7	0.18	0.59	0.06	274.1	1.85	2.60
2.60	121.8	0.27	0.96	0.10	264.6	2.73	3.33
3.63	120.8	0.52	1.41	0.16	263.6	3.83	3.68
4.41	116.7	0.76	1.78	0.21	261.9	4.61	-
5.27	112.9	0.95	2.20	0.27	257.0	5.23	-

ΔP mm Hg	CH_3 CHO		C_2H_5 CHO		CH_3CO CH_3	CH_3 OH	O_2	CO
1.15	0.17	0.00	0.22	0.05	0.44	0.00	140.2	0.28
2.19	0.24	0.05	0.36	0.09	0.54	0.00	122.5	0.40
3.14	0.35	0.06	0.57	0.18	0.85	0.24	121.9	0.60
4.26	0.46	0.09	0.87	0.31	1.11	0.37	117.1	0.84
5.37	0.60	0.10	0.98	0.41	1.51	0.63	116.7	1.06
6.48	0.81	0.12	1.34	0.60	2.01	0.83	110.8	1.30
7.70	0.91	-	1.59	0.72	2.16	1.02	107.2	1.67
8.96	0.99	0.13	1.61	0.80	2.73	0.98	102.6	1.97
10.21	1.13	0.16	1.70	1.07	3.36	1.53	101.0	2.65
12.03	1.22	0.17	1.62	1.08	4.11	1.66	-	-

Table 11A

Element Balances Temp = 330°C Isobutane:Oxygen = 2:1 Pressure = 100 mm

ΔP	mm atoms			Total R.V.	H_2O(calc)	mm atoms	Pressure
mm	C	H	O	Pressure(mm)	mm	H (calc)	mm (calc)
0	254	635	69	98	-	-	-
2	239	610	61.6	92.7	7.4	625	100
4	244	593	55.5	88.7	13.5	620	102.1
5	242	584	52.4	86.7	16.6	618	103.0
6	242	580	49.6	85.2	19.4	620	104.6
8	241	571	43.3	82.0	25.7	623	107.7
10	242	566	38.0	79.7	31.0	628	110.0

Table 12A

Element Balances Temp = 270°C Isobutane:oxygen = 2:1 Pressure = 400 mm

ΔP	mm atoms			Total R.V.	H_2O(calc)	mm atoms	Pressure
mm	C	H	O	Pressure(mm)	mm	H (calc)	mm (calc)
0	1088	2720	264	404	-	-	-
1	1084	2706	260.3	401.9	3.7	2714	405.6
2	1082	2697	255.2	397.8	8.8	2715	406.6
3	1080	2688	250.6	394.7	13.4	2715	408.1
4	1079	2680	246.3	392.2	19.7	2720	411.9

Note: Experimental water values are not included in either the oxygen or pressure balances.

Table 13 (Figures 15-22)

Initial fractional yields of products (in mm atom C of product per mm atom of C in total product).

Initial Pressure = 200 mm Temp = 300°C Katharometer Detection.

Isobutane / Oxygen	0.5	1	2	4	9
Mixture	A	B	C	D	E
Carbon Monoxide	0.043	0.039	0.048	0.032	0.017
Carbon Dioxide	0.077	0.080	0.062	0.039	0.036
Propylene	0.025	0.048	0.043	0.051	0.042
Isobutene	0.55	0.62	0.71	0.73	0.80
Acetaldehyde	0.053	0.042	0.027	0.025	0.017
Isobutene Oxide	0.023	0.026	0.011	0.055	0.028
Propionaldehyde	0.073	0.046	0.020	0.042	0.020
Acetone	0.155	0.084	0.089	0.074	0.065

Table 14 (Figures 23-27)

Initial fractional yields of products (in mm atom C of product per mm atom C in total product).

Isobutane:Oxygen = 2:1 Katharometer Detection.

Temperature	270	300	330
Initial Pressure (mm)	260	200	100
Mixture	M	L	K
Carbon Monoxide	0.015	0.050	0.035
Carbon Dioxide	0.050	0.062	0.033
Propylene	0.028	0.043	0.055
Isobutene	0.64	0.72	0.80
Acetaldehyde	0.031	0.027	0.026
Isobutene Oxide	0.048	0.011	0.020
Propionaldehyde	0.079	0.020	0.026
Acetone	0.105	0.089	0.064

Table 15 (Figure 6)

$iC_4H_{10}:O_2$ ratio = 2:1 Pressure = 200 mm Temp = 300°C

ΔP mm Hg	4.28	6.30	10.0	11.66	18.51	21.34	22.98
CH_2O mm Hg	1.48	2.79	4.21	4.96	6.79	6.73	6.74

Table 16 (Figure 11)

$iC_4H_{10}:O_2$ ratio = 2:1 Pressure = 100 mm Temp = 330°C

ΔP mm Hg	1.24	2.33	2.79	5.21	7.42	9.34	12.69	14.98
CH_2O mm Hg	0.49	0.83	0.83	1.43	2.00	2.33	2.85	2.88

Table 17

$iC_4H_{10}:O_2$ ratio = 2:1 Pressure = 200 mm Temp = 300°C

ΔP mm Hg	8.00	8.68	9.42	13.64
H_2O_2 mm Hg	0.17	0.51	1.39	0.27

2) Low isobutane conversion studies using flame ionisation detection for analysis.

As demonstrated in the previous section, secondary oxidation of products occurs as the reaction proceeds and distinction between primary and secondary products is not easy. Studies were carried out on the initial stages of isobutane oxidation where the conversion of the alkane is in the range 0-2%. Under such conditions, only primary products should be formed. Since neither pressure rise nor time is a reliable indication of the extent of reaction in the very early stages, the extent of reaction was measured by the mm atoms carbon of the total product. In this series of runs, samples taken at any given time were analysed for both hydrocarbons and oxygenated compounds and product pressures were calculated. The total carbon content of the products is the sum over all products of product pressure multiplied by the number of carbon atoms per product. The values plotted in Figures 29-36 are experimental values while the values of carbon content used in the previous section were derived from composite product pressure against ΔP graphs. The initial product yields found here will differ from those of section 1, as carbon oxides, which are insensitive to flame ionisation detection, are not included in the carbon content of the total product.

The effect of mixture composition on the initial yields of products was studied at 300°C using a fixed pressure of isobutane, 150 mm, and variable oxygen pressures. Since the initial products of alkane oxidations must arise from the reactions of alkyl radicals and oxygen, isobutane pressure should have no effect on the initial product yields. Accordingly, only the effect of oxygen pressure on the initial product yield has been investigated. A five-fold change in isobutane:oxygen ratio was studied using mixtures of initial pressures 225 mm, 187.5 mm, and 165 mm. The results of these oxidations are listed in Tables 18-20 and illustrated in Figures 29-32. A similar set of experiments was carried out at 270°C on 2:1 and 1:1 isobutane:oxygen mixtures at 225 mm and

300 mm initial pressure. Tables 23 and 24 show the results which are illustrated in Figures 33-36. Products detected were isobutene, propylene, ethylene, acetaldehyde, propylene oxide, isobutene oxide, propionaldehyde, isobutyraldehyde, acetone, methacrolein, methanol and an unidentified minor oxygenated compound which was eluted after methanol. The yields of all products approached the X-axis with a finite gradient indicating that all products are initial products, the only possible exception being the yield of isobutene oxide at 270°C (Figure 33). In this case, the X-axis acts as a tangent to the isobutene oxide curve, indicating that isobutene oxide may be a secondary product. Generally, the dependence of the initial yield of any product on oxygen pressure is slight. The main features of the initial product yields agree well with those found in the initial stages of the overall reaction.

1) the initial yield of isobutene decreases as the oxygen pressure rises.
2) the initial yields of acetaldehyde and propionaldehyde increase with oxygen pressure while those of isobutyraldehyde and methacrolein decrease with increase in oxygen.
3) Isobutene oxide, propylene and acetone yields are independent of oxygen.

The yields of minor products, propylene oxide, ethylene and methanol, although included in the carbon content of the total product, have not been plotted. Table 25 summarises the oxygen dependences of initial product yields at 300°C.

Temperature dependence of initial yields has been studied by oxidising a 2:1 mixture of isobutane:oxygen at 330°C and 100 mm pressure and comparing the initial product yields with those obtained from the 2:1 isobutane:oxygen mixture oxidations at 270°C (Table 23) and 300°C (Table 18). The results of the comparisons are shown in Figures37-40 and the initial product pressures for the oxidation at 330°C are given in Table 26. Temperature effects, although again generally slight are more complicated than expected. Initial isobutene yield is

independent of temperature while the initial yields of isobutene oxide and propylene rise with increase in temperature. Acetone yield decreases with temperature. Initial yields of aldehydes show particularly unusual behaviour. Acetaldehyde and propionaldehyde initial yields exhibit maxima while the initial yields of isobutyraldehyde and methacrolein go through minima. Only the initial yields of propylene and acetone can be roughly fitted to an Arrhenius equation. The initial yields of aldehydes clearly do not fit such an equation. The activation energy for the reaction forming isobutene is 11 $\pm$ 2 k cal higher than that forming acetone while the activation energy for the reaction forming propylene is 7 $\pm$ 2 k cal greater than that forming isobutene. These differences are in agreement with those obtained from katharometer data on the overall reaction. Table 27 lists the variations with temperature of the initial product yields.

Mixtures to which a) nitrogen at a pressure equal to that of the initial oxygen and b) isobutene equivalent to 1% of the initial isobutane had been added were oxidised at 270°C in separate sets of experiments. This temperature was selected for this study as the results of oxidations at 270°C are extremely reproducible. This high degree of reproducibility is shown in curves P of Figures 33-36, in which the experimental points were obtained from four separate oxidations. Addition of inert gas decreases the importance of products which may be influenced by diffusion of radicals to the walls of the reaction vessel. A 2:1:1 mixture of isobutane:oxygen:nitrogen at 300 mm pressure was oxidised in two separate runs. Reproducible results were obtained. Pressures of products are shown in Table 28 and the initial yields of products are described in Figures 33-36. Again, no drastic alteration in the initial yields of products was observed. A small increase in the initial yield of isobutene was accompanied by slight decreases in the initial yields of oxygenated compounds. Addition

of inert gas actually caused an increase in the initial yield of propionaldehyde.

Olefins often act as promoters of alkane oxidations, as, since they are more easily oxidised than alkanes, they provide an additional source of free radicals. The initial yield of products which result from secondary oxidation of isobutene should be greater in mixtures containing added isobutene than in pure isobutane:oxygen mixtures. Two oxidations were carried out at 270°C in which 1% (1.5 mm) of the isobutane was replaced by isobutene. The duration of the induction period was greatly reduced. Results shown in Table 29 and Figures 33-36 indicate that the initial yields of isobutene were reduced while those of the oxygenated compounds were increased. The outstanding features of the results are the increases in the initial yields of isobutene oxide and propionaldehyde, whose initial yields are higher by factors of four and two respectively than those obtained when no isobutene had been added to the initial mixture. When 1.5 mm (6 mm atom Carbon) of isobutene have been formed in the unpromoted oxidation (curve P, Figure 33), the carbon content of the total product can be determined from the graph. The rate of production of an oxygenated compound (e.g. isobutene oxide) at a carbon content corresponding to the formation of 1.5 mm of isobutene can be measured by taking the gradient of the tangent to the isobutene oxide curve at a point where the total carbon content is that which contains 6 mm atoms carbon of isobutene. In mixed oxidations, the initial yields of products which are formed from isobutene may be expected to be equal to the rates of production of these products in unpromoted oxidations at a carbon content corresponding to the formation of the amount of isobutene which has been added in the mixed oxidation. The initial yields of isobutene oxide and propionaldehyde in the promoted oxidations (Figures 33 and 35, curves S and T) are close to the rates of production observed in isobutane-oxygen mixtures in which 1.5 mm of

isobutene haa been formed. This increase in the initial yield of isobutene oxide supports the suggestion that the formation of isobutene oxide in isobutane oxidation may result from oxidation of isobutene formed. However, work by Hay and Knox [79] has shown that propionaldehyde is not an initial product of isobutene oxidation at 300°C.

The results of all oxidations studied at 270°C have been compared in Figures 33-36 and the initial product yields listed in Table 30.

Figure 41 shows a plot of log (product pressure) against time for Run 52, an oxidation of a 2:1 isobutane:Oxygen mixture at 270°C at 225 mm pressure. Oxidations carried out at this temperature have long induction periods and no pressure increase occurs until the reaction has been in progress for four hours. The straight lines in Figure 41 indicate that products are formed exponentially with time during the induction period. That similar development occurs in the early stages of a similar oxidation at 270°C is shown in Figure 42.

After oxidations at 270°C had been carried out (Runs 49-54), the reaction vessel was cooled to room temperature and mixtures of isobutane, isobutene oxide and nitrogen allowed to pass through it. On raising the temperature to 330°C and oxidising 2:1 isobutane:oxygen mixtures at 100 mm pressure, unusual results were obtained (Table 31, Figures 43-45). The initial isobutene yield was in marked contrast to that expected, being only 60% of the carbon content of the total product and the yields of oxygenated compounds, particularly isobutene oxide (15%), were abnormally high. Isobutene oxide appeared to be formed as an product alternative to isobutene. In successive runs (Figures 43-45) the initial yield of isobutene increased gradually towards the expected initial yield of 80% while the yields of oxygenated compounds gradually decreased. The variations of initial product yields are shown in Table 32. As these trends indicated that the condition of the reaction vessel surface was gradually

changing, several oxidations were carried out, without analysis, in an attempt to restore the reaction vessel to its original condition. After a few days the temperature was lowered to 300°C and a 4:1 mixture of isobutane: oxygen oxidised at 187.5 mm pressure (Runs 59-60). The analytical results were compared to those of previous oxidations under the same experimental conditions (Figures 29-32, Table 21). Although not identical to those obtained previously, the results indicated that the reaction vessel surface had been restored to its original condition. A 4:1 isobutane:oxygen mixture at 100 mm pressure was oxidised at 330°C. No odd effects were observed, the initial yields of isobutene and isobutene oxide being 80% and 5% respectively (Table 33). Thus, the 2:1 isobutane:oxygen oxidations at 330°C which were used for the determination of the temperature dependence of the initial product yields were next carried out. Table 22 shows the product pressures from a check oxidation of a 10:1 isobutane:oxygen mixture at 300°C, the product yield curves of which are incorporated in Figures 28-31. Table 34 below lists all the tables and figures containing data from low isobutane consumption oxidations carried out in a clean Pyrex reaction vessel over a range of experimental conditions.

Table 34

Run Nos.	Temp. °C	Isobutane (mm)	Oxygen (mm)	Nitrogen (mm)	Isobutene (mm)	Table Nos.	Figure Nos.
29-31	300	150	75	-	-	18	29-32
33-35	300	150	37.5	-	-	19	29-32
37-39	300	150	15	-	-	20	29-32
49-52	270	150	75	-	-	23	33-36
53-54	270	150	150	-	-	24	33-36
55-58	330	67	33	-	-	31	43-45
59-60	300	150	37.5	-	-	21	29-32
61	330	80	20	-	-	33	-
62-63	330	67	33	-	-	26	37-40
64	300	150	15	-	-	22	29-32
73-74	270	150	75	75	-	28	33-36
75-76	270	150	75	-	1.5	29	33-36

The general results of the initial stages oxidations showed that the mechanism of product formation is by no means simple. Experiments described in the second half of this section have suggested that the initial yields of the minor products are dependent on the nature of the reaction vessel surface. Accordingly, oxidations have been carried out in coated reaction vessels and the effects of acidic and alkali coatings are described in section 4 of the experimental results.

Table 18 (Figures 29-32)

$iC_4H_{10}:O_2$ ratio - 2:1 Pressure - 225 mm Hg Temp = 300°C

Pressure in Reaction Vessel (mm Hg x 10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_3CH\overset{O}{\diagdown}CH_2$	$(CH_3)_2C\overset{O}{\diagdown}CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	Sample No.
436	1.6	24.6	17.0	1.4	16.7	21.0	5.9	13.5	2.9	29/1
830	3.8	52.8	60.2	3.8	54.2	69.7	21.6	47.8	6.5	29/2
1364	8.0	100.6	89.6	8.1	86.2	99.8	39.9	88.9	12.8	29/3
2240	16.9	190	188.6	18.7	191	206	68.9	175.8	25.2	29/4
3050	38.7	329	277	32.2	340	290	87.2	289	38.1	29/5
298	1.7	17.1	20.3	1.0	19.1	24.0	6.5	14.4	2.6	30/1
770	3.5	47.7	47.8	2.3	44.6	55.0	16.9	33.6	7.1	30/2
1378	8.5	105.0	94.7	5.9	95.9	106.4	35.7	82.2	15.5	30/3
2090	18.8	200.0	140.0	9.5	137.2	142.0	49.3	121.1	17.7	30/4
2354	36.0	322.0	234.0	23.3	304	251.7	72.3	267.5	38.3	30/5
308	1.6	17.0	15.7	0.7	15.3	21.8	7.5	13.5	2.6	31/1
701	3.4	41.7	44.1	2.0	41.7	58.0	17.8	35.5	6.3	31/2
1279	7.8	91.8	98.0	5.3	85.3	103.1	34.5	69.7	12.9	31/3
1794	17.0	154.4	142.6	11.2	133.2	148.2	47.9	108.7	19.6	31/4
3048	43.3	379.0	272.0	24.0	326	284.3	78.9	277.5	38.5	31/5

Table 19 (Figures 29-32)

$iC_4H_{10}:O_2$ ratio = 4:1 Pressure = 187.5 mm Temp = 300°C

Pressure in Reaction Vessel (mm Hg x 10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_2{-}CH{-}CH_2$ (O)	$(CH_3)_2C{-}CH_2$ (O)	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	Sample No.
334.8	-	12.8	-	-	-	-	-	-	-	33/1
677.7	-	23.7	30.5	1.8	29.1	34.5	28.5	38.1	13.3	33/2
845	-	37.5	43.8	3.3	40.8	47.5	40.3	51.5	22.1	33/3
1051	-	51.0	57.5	4.4	57.0	59.9	48.5	74.4	25.4	33/4
1543	-	83.4	77.5	5.9	72.3	80.4	70.7	105.7	39.1	33/5
223.0	-	7.3	7.6	1.1	13.3	9.8	6.1	7.7	2.8	34/1
498	-	16.6	19.8	1.3	25.6	23.7	17.5	20.4	7.4	34/2
633	-	32.1	38.0	2.8	42.9	44.6	37.0	40.9	15.8	34/3
1243	-	57.4	61.3	5.8	75.2	65.4	53.0	69.4	23.3	34/4
1795	-	82.1	95.2	9.8	126.9	96.6	78.9	120.9	37.2	34/5
287	-	9.5	9.2	0.6	14.5	11.8	7.9	8.8	3.6	35/1
523	-	21.4	22.9	1.4	28.6	27.3	21.2	22.5	9.6	35/2
-	-	-	41.7	2.2	57.0	48.0	32.6	43.6	15.9	35/3
1234	-	52.1	61.9	4.8	93.5	70.9	48.2	68.7	24.5	35/4
1592	-	93.5	86.1	8.2	136.4	90.3	62.0	103.3	31.5	35/5

Table 20 (Figures 29-32)

$iC_4H_{10}:O_2$ ratio = 10:1 Pressure = 165 mm Hg Temp = 300°C

Pressure in Reaction Vessel (mm Hg x 10^3)

iC_4H_8	C_3H_6	CH_3CHO	$CH_3CH(O)CH_2$	$(CH_3)_2C(O)CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	Sample No.
215.6	7.5	3.7	0.0	9.1	4.3	6.6	6.1	3.6	37/1
448	19.2	9.9	0.8	14.0	10.1	17.8	18.5	11.6	37/2
682	30.4	12.7	1.4	19.2	14.2	26.9	27.1	16.8	37/3
919	45.1	19.0	1.6	23.0	18.0	37.6	41.5	26.4	37/4
1277	66.3	28.4	3.1	41.9	26.4	57.5	73.5	42.4	37/5
104.6	3.3	1.5	0.0	4.9	2.0	2.7	3.6	1.7	38/1
207.8	4.5	2.9	0.0	7.3	4.0	6.8	6.1	4.4	38/2
356	8.2	6.7	0.8	12.5	8.1	14.5	12.0	9.4	38/3
521	15.1	10.2	1.2	16.3	11.5	21.8	21.9	15.3	38/4
872	32.5	18.2	2.2	29.8	19.2	37.5	51.5	27.1	38/5
264.8	5.4	4.8	0.0	11.8	6.2	10.4	9.3	6.4	39/1
510	14.3	11.2	1.3	20.8	11.3	20.9	21.0	13.1	39/2
757	21.6	19.4	2.4	39.5	20.1	36.1	40.1	25.6	39/3
965	29.0	27.5	3.1	52.9	24.9	46.7	55.9	31.9	39/4
1216	36.7	34.2	3.9	73.8	30.6	59.6	75.6	43.7	39/5

Table 21 (Figures 29-32)

isoButane:Oxygen = 4:1 Pressure = 187.5 mm Hg Temp = 300°C

Pressure in Reaction Vessel (mm Hg×10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_3CH\text{-}CH_2$ (O)	$(CH_3)_2C\text{-}CH_2$ (O)	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	CH_3OH	X	Sample No.
667	2.8	56.5	36.7	3.3	50.0	39.1	20.6	45.6	5.9	35.1	4.3	59/1
1149	5.8	116.5	66.7	8.8	94.8	73.5	43.4	88.8	12.4	73	11.3	59/2
1669	10.6	196	104.4	15.5	164	109	59.4	157	18.3	131	11.2	59/3
2197	17.7	287	140.4	25	271	146	71	222	26.7	134	18.8	59/4
2744	26.7	386	180	36.9	365	172	84	313	37.1	217	26.4	59/5
332	1.4	20	12.2	0.7	26.1	17.2	5.1	20	2.8	0.0	0.0	60/1
696	2.7	50	31.5	1.9	54.4	40.6	15.4	36.3	5.9	33.9	3.9	60/2
1050	5.2	83	51.8	3.2	94.1	66.2	27.5	61.0	12.4	59.2	4.1	60/3
1524	9.5	142	73.4	5.3	144	97.1	38.1	91	16.9	73.7	5.5	60/4
2005	18.1	216	103	9.0	232	136	54.1	142	27.4	121	9.9	60/5

Table 22 (Figures 29-32)

isoButane:Oxygen = 10.1 Pressure = 165 mm Temp = 300°C

Pressure in Reaction Vessel (mm Hg x 10^3)

Ethylene	0.8	1.3	1.5	2.5	3.4
Propylene	10.5	20.9	37.3	58.6	80.5
Isobutene	236.4	388.6	627	887	1114
Acetaldehyde	5.3	9.2	15	21.8	28.5
Propylene Ox.	0.0	0.0	1.3	2.0	2.7
Isobutene Ox.	15.4	26.0	46.3	67.1	97.2
Propionaldehyde	4.5	10.8	19.4	27.7	36.2
Isobutyraldehyde	6.2	12.5	21.7	30.0	42.1
Acetone	5.9	11.8	23.0	32.5	46.4
Methacrolein	3.3	5.2	10.3	12.0	18.6
Sample No.	64/1	64/2	64/3	64/4	64/5

Table 23 (Figures 33-36)

iC_4H_{10}:O_2 ratio = 2:1 Pressure = 225 mm Hg Temp = 270°C

Pressure in Reaction Vessel (mm Hg x 10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_3CH\overset{O}{\diagdown}CH_2$	$(CH_3)_2C\overset{O}{\diagdown}CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	CH_3OH	X	Sample No.
2897	52.9	198.7	155.8	37.4	247.6	324	76.5	347	28.7	237	44.0	49/1
3135	58.0	221	173	40.4	284	359	85.4	389	31.4	277	47.2	49/2
3401	66.0	256	191	43.1	343	399	88.1	454	33.7	231	47.9	49/3
3634	75.4	279	211	47.9	381	428	97.6	510	36.2	292	50.1	49/4
3820	88.8	329	226	50.3	422	468	96.6	596	40.3	302	58.9	49/5
1107	6.9	40.8	57.7	14.8	20.6	75.4	43.1	151.1	13.9	180	26.0	50/1
1300	9.2	52.5	63.8	18.3	29.1	97.4	44.2	137	16.1	117	24.3	50/2
1469	12.1	61.5	75.4	22.3	42.5	120.9	50.9	154	18.3	77	28.4	50/3
1640	14.8	73.4	83.8	23.6	52.5	138.6	56.1	171	19.2	94	30.7	50/4
1862	19.3	85.0	92.7	28.0	71.6	161.1	64.9	192	21.3	71	36.6	50/5
2456	28.4	131.9	128.2	32.7	165.6	276	74.2	294	23.4	167	32.6	51/1
2692	34.8	155.7	137	34.3	193	305	73.3	301	24.8	148	33.5	51/2
2913	39.9	187.5	159	38.5	239	347	80.3	358	27.9	179	38.2	51/3
3101	48.9	210.0	170	39.9	259	361	78.8	385	28.3	188	38.2	51/4
3369	57.0	237	188	43.0	319	408	87.6	443	33.2	227	47.8	51/5
402	2.0	13.2	19.9	4.3	3.0	21.9	15.1	66.4	9.2	72	9.0	52/1
653	3.0	19.0	27.3	6.8	4.3	28.8	16.0	64.3	7.8	64	8.2	52/2
1030	5.7	36.4	52.1	15.1	16.0	70.5	33.3	108.3	14.7	69	20.7	53/3
1532	11.6	65.1	77.7	21.9	40.0	121	51.2	154	17.8	89	25.1	54/4
1910	18.5	89.0	93.3	27.8	72.1	168	64.3	193	22.5	63	29.5	54/5

Table 24 (Figures 33-36)

$iC_4H_{10}:O_2$ ratio = 2:1 Pressure = 300 mm Temp = 270°C

Pressure in Reaction Vessel (mm Hg x 10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_3CH(O)CH_2$	$(CH_3)_2C(O)CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	CH_3OH	X	Sample No.
876	4.9	21.1	50.1	12.1	15.3	80	27.2	96.5	8.4	122	13.2	53/1
1277	8.3	36.2	69.6	20.5	34.4	130	33.6	116.2	10.4	73.6	20.7	53/2
2329	26.8	96.4	144.3	42.4	140.5	315	59.4	258.2	16.1	117	34.4	53/3
2534	32.3	111.7	157.7	43.6	154.9	332	58.4	278.3	15.6	105	31.2	53/4
2850	42.3	137.8	170.0	49.6	212.6	402	67.4	346.3	20.0	120	39.1	53/5
1701	12.5	47.6	82.3	15.0	50.4	181	40.2	184.4	12.7	128	19.0	54/1
2011	21.0	73.7	103.3	20.0	90.8	268	41.3	200.3	13.4	122	23.3	54/2
2269	26.0	89.1	117.8	22.6	119.1	316	44.3	224.1	14.2	122	29.8	54/3
2501	32.2	101.0	138.3	23.8	143.0	351	47.3	257	14.7	118	30.3	54/4
2786	41.5	135.3	152.8	27.2	184.5	408	52.4	308	18.1	138	35.0	54/5

Table 25 (Figures 29-32)

Dependence of initial yields of products on oxygen pressure.

Temp = 300°C Isobutane = 150 mm Flame ionisation detection.

Code letter	A	B	C	D	E	F
Run Nos.	29-31	33-35	37-39	59	60	64
Oxygen (mm)	75	37.5	15	37.5	37.5	15
Initial yields						
Isobutene	0.80	0.82	0.84	0.76	0.77	0.82
Propylene	0.034	0.025	0.028	0.034	0.036	0.033
Acetaldehyde	0.026	0.019	0.009	0.021	0.017	0.011
Isobutene Oxide	0.045	0.039	0.024	0.055	0.061	0.051
			Run 39 0.037			
Propionaldehyde	0.044	0.031	0.013	0.031	0.033	0.036
Isobutyraldehyde	0.018	0.031	0.036	0.024	0.018	0.029
Acetone	0.027	0.032	0.031	0.039	0.032	0.024
Methacrolein	0.007	0.016	0.026	0.008	0.008	0.011

Table 26 (Figures 37-40)

Isobutane:Oxygen = 2:1 Pressure = 100 mm Temp = 330°C

Pressure in Reaction Vessel (mm Hg x 10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_3CH\overset{O}{\diagdown\diagup}CH_2$	$(CH_3)_2C\overset{O}{\diagdown\diagup}CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	CH_3OH	X	Sample No.
629	4.2	47.9	30.5	2.1	61.7	21.3	21.9	21.3	11.1	15.3	0.0	62/1
1305	10.5	136	70.2	4.7	166	54.5	46.7	53.5	28.4	35.3	0.0	62/2
1995	26.5	261	124	10.3	336	93.6	78.7	118	55.4	89.9	3.9	62/3
2849	44.1	443	182	18.8	558	123	97.5	218	78.8	152	8.9	62/4
4070	81.2	724	249	33.2	918	154	120	401	131	215	10.1	62/5
119	0.7	4.1	6.2	0.0	11.3	3.6	3.7	7.1	3.2	0.0	0.0	63/1
315	0.7	11.7	13.4	0.0	23.3	8.0	10.6	7.3	6.5	0.0	0.0	63/2
567	2.0	23.7	26.6	1.3	44.1	15.9	21.8	12.5	14.0	13.9	0.0	63/3
847	3.8	44.1	47.1	1.8	76.2	24.7	32.3	20.4	20.4	0.0	0.0	63/4
1191	7.3	73.6	59.6	2.8	135	41.0	49.0	39.4	35.0	43.3	0.0	63/5

Table 27 (Figures 37-40)

Dependence of initial product yields on temperature.

Isobutane:oxygen = 2:1 Flame ionisation detection.

Code letter	K	L	M	N
Temperature °C	270	300	330	330
Pressure (mm)	225	225	100	100
Run Nos.	49-52	29-31	62	63
Initial Yields				
Isobutene	0.80	0.80	0.79	0.80
Isobutene oxide	0.008	0.045	0.073	0.061
Acetone	0.056	0.027	0.023	0.020
Propylene	0.021	0.034	0.041	0.029
Acetaldehyde	0.018	0.026	0.019	0.020
Propionaldehyde	0.034	0.044	0.020	0.019
Isobutyraldehyde	0.028	0.018	0.028	0.030
Methacrolein	0.010	0.007	0.016	0.018

Table 28 (Figures 33-36)

$iC_4H_{10}:O_2:N_2$ = 2:1:1 Pressure = 300 mm Hg Temp = 270°C

Pressure in Reaction Vessel (mm Hg x 10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_3CH(O)CH_2$	$(CH_3)_2C(O)CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	CH_3OH	X	Sample No.
122.6	1.0	1.6	3.4	0.0	1.0	6.4	3.9	9.5	1.2	-	-	73/1
186.9	1.0	3.7	4.2	1.0	1.3	10.3	4.9	11.5	1.7	20.7	6.1	73/2
233.3	1.2	4.6	6.6	1.1	1.0	14.5	7.4	15.7	3.3	-	-	73/3
875.3	4.3	27.2	30.5	4.6	7.2	65.6	28.4	59.3	8.9	30.9	14.3	73/4
1325	10.1	53.1	43.0	7.6	2.9	95.9	49.8	102.6	11.6	60.6	18.7	73/5
325.6	1.2	6.8	11.4	2.0	2.2	23.3	12.0	30.0	2.1	24.9	6.1	74/1
584	2.7	14.4	19.3	2.8	3.2	41.9	18.4	42.5	6.3	24.1	9.1	74/2
906	4.5	28.1	33.3	5.2	6.8	70.4	30.0	74.7	9.8	41.0	13.0	74/3
1267	8.0	48.7	49.9	7.1	12.5	106.0	44.1	100.7	12.8	58.8	18.1	74/4
1845	17.7	80.2	71.0	11.3	19.7	148.4	70.3	154.5	17.0	79.8	22.1	74/5

Table 29 (Figures 33-36)

iC_4H_{10} = 148.5 mm , iC_4H_8 = 1.5 mm , O_2 = 75 mm

Pressure = 225 mm Temp = 270°C

Product Pressure in Reaction Vessel (mm Hg x 10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_2\overset{\delta}{\underset{\delta}{CH}}-CH_2$	$(CH_3)_2C\overset{O}{\underset{O}{}}-CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	CH_3OH	X	Sample No.
261	1.6	15.7	10.3	1.0	22.6	43.0	8.6	28.0	0.0	18.3	11.1	75/1
487	2.8	34.8	24.5	2.0	42.2	88.0	16.8	63.0	3.7	30.5	14.9	75/2
684	4.3	55.6	46.9	3.0	70.4	142.2	25.1	110.7	4.7	57.3	22.2	75/3
1015	7.4	98.9	78.2	5.1	93.0	205	40.7	184.5	7.2	90.0	22.9	75/4
1479	15.0	163	124.6	7.9	139.1	293	66.4	325	11.6	183.0	48.7	75/5
712	4.2	29.1	35.3	12.0	30.0	85.6	55.5	92.5	8.7	59.4	68.0	76/1
2663	42.8	222	171.5	34.2	272	434	122.6	482	29.9	229	46.5	76/2
3003	52.0	284	202	43.1	329	477	131	568	35.6	305	50.1	76/3
3258	69.8	344	261	48.2	452	582	139	773	41.0	411	60.1	76/4
3770	85.5	443	324	55.4	503	659	168	971	50.1	497	77.1	76/5

Table 30 (Figures 33-36)

Comparison of initial product yields under differing conditions at 270°C.

Isobutane = 150 mm

Oxygen (mm)	75	150	75	75	75
Nitrogen (mm)	-	-	-	-	-
Isobutene (mm)	-	-	-	1.5	1.5
Run Nos.	49-52	53-54	73-74	75	76
Key Letter	P	Q	R	S	T
Initial Yields					
Isobutene	0.80	0.77	0.85	0.67	0.70
Isobutene Oxide	0.008	0.011	0.007	0.028	0.042
Acetone	0.056	0.053	0.045	0.062	0.064
Propylene	0.021	0.016	0.021	0.040	0.022
Acetaldehyde	0.018	0.020	0.014	0.022	0.016
Propionaldehyde	0.034	0.053	0.047	0.087	0.061
Isobutyraldehyde	0.028	0.020	0.027	0.026	0.050
Methacrolein	0.010	0.008	0.007	0.003	0.006

Table 31 (Figures 43-45)

Isobutane:Oxygen ratio = 2:1 Pressure = 100 mm Hg Temp = 330°C

Pressure in Reaction Vessel (mm Hg x 10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_3CH\overset{O}{\diagdown}CH_2$	$(CH_3)_2C\overset{O}{\diagdown}CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	CH_3OH	X	Sample No.
579	2.5	55.6	47.8	1.2	113	14.3	2.5	23.8	11.9	35	0.0	55/1
1949	10.8	286	197.2	9.1	501	63.9	26.7	144.3	53.5	130	7.7	55/2
3908	41.1	888	484	44.0	1445	113.3	68.5	599	62.3	-	-	55/3
6154	100.2	1735	741	134.7	2840	142	105	1617	112	-	-	55/4
536	1.4	39.1	40.1	1.1	103	70	10.0	24.6	9.4	19.6	0.0	56/1
1218	3.6	116	103.3	3.5	268	18.7	32.0	72	28.4	67	7.6	56/2
2046	8.1	247	189	8.9	593	34.7	45.6	158	58.8	87	12.6	56/3
3041	19.3	590	330	22.0	1104	50.7	77.3	358	104.7	190	18.8	56/4
4108	31.9	712	367	39.6	1588	57.9	80.1	569	151.8	244	24.1	56/5
549	1.6	42.3	40	0.0	98	7.8	5.4	19.7	9.9	22.8	0.0	57/1
1261	4.2	131.3	103	3.2	283	22.6	20.2	64	27.9	49	8.5	57/2
2340	11.4	324	211	10.3	613	36.9	39.2	179	64.4	120	10.2	57/3
3377	22.0	582	305	24.4	1070	47.5	64.1	376	107.4	222	17.5	57/4
4534	38.0	936	389	48.5	1642	57.8	62.3	637	158	364	30.6	57/5
428	1.8	29	26	0.9	64	12.4	9.2	11.3	8.4	18.4	0.0	58/1
1103	5.9	112	71	3.5	219	40.5	21.2	46.9	26.8	28.7	2.2	58/2
2163	21.4	302	146	10.0	525	76.1	35.8	138	59.5	91	5.6	58/3
3375	54.7	629	249	27.4	1058	120	55.3	362	110.7	302	10.1	58/4
4821	115.1	1107	351	62.9	1620	148	72.2	761	179	364	17.4	58/5

Table 32 (Figures 43-45)

Variation of initial product yields in successive runs at 330°C

Isobutane:oxygen = 2:1 Temp = 330°C Pressure = 100 mm

Run No.	55	56	57	58
Code letter	K	L	M	N
Initial Yields				
Isobutene	0.64	0.67	0.70	0.72
Isobutene Oxide	0.152	0.159	0.146	0.140
Acetone	0.037	0.031	0.030	0.027
Propylene	0.056	0.047	0.056	0.050
Acetaldehyde	0.035	0.030	0.028	0.021
Propionaldehyde	0.015	0.009	0.008	0.018
Isobutyraldehyde	0.008	0.016	0.012	0.011
Methacrolein	0.012	0.016	0.017	0.017

Table 33

Isobutane:oxygen = 4:1 Pressure = 100 mm Hg Temp = 330°C

Pressure in Reaction Vessel (mm Hg x 10^3)

Ethylene	0.9	1.2	2.1	4.2	6.2
Propylene	11.4	21.4	33.3	59.4	86.5
Isobutene	301	488	694	1014	1306
Acetaldehyde	0.9	1.1	2.4	3.0	4.8
Propylene Ox.	0.6	0.7	1.7	2.1	3.4
Isobutene Ox.	15.1	24.0	39.8	63.1	97.9
Propionaldehyde	4.9	8.4	13.2	18.4	26.3
Isobutyraldehyde	13.8	22.5	34.6	49.6	63.0
Acetone	9.4	14.2	22.7	31.1	46.1
Methacrolein	8.5	14.9	24.5	34.5	47.9
Methanol	-	-	-	-	34.2
X	-	-	-	-	3.4
Sample No.	61/1	61/2	61/3	61/4	61/5

3. Oxidation of Propane:Isobutane Mixtures.

2:1:1 mixtures of propane:isobutane:oxygen were oxidised at 300°C at 200 mm pressure. The initial stages of the reactions were again examined using flame ionisation detection for analysis. The relative rates of consumption of the alkanes were measured by the ratios of products characteristic of the individual alkanes, the olefin of the same carbon number being taken in both cases. Rate constant ratios were calculated from the formula

$$\frac{k\ (\text{isobutane})}{k\ (\text{propane})} = \frac{[iC_4H_8][C_3H_8]}{[C_3H_6][iC_4H_{10}]}$$

The rate constant for radical attack on isobutane was found to be 2-3 times greater than the rate constant for radical attack on propane at 300°C. Tables 35 and 36 contain experimental results of the competitive oxidations. The nature of the radical attacking the hydrocarbons and the accuracy of this method compared to that used by Knox, Falconer and Trotman-Dickenson [74] will be considered in the discussion.

Table 35

Isobutane:Propane:Oxygen = 2:2:1 Pressure = 200 mm Temp = 300°C

Pressure in Reaction Vessel (mm Hg x 10^3)

Run 42	Initial Mixture	Sample 1	Sample 2	Sample 3	Sample 4
Ethylene	349	341	346	352	358
Propylene	231.7	266.1	320.8	450.7	532.0
Propylene formed	0.0	34.4	89.1	219.0	300.3
Isobutene formed	0.0	145.9	327.0	575.3	771.4
Propylene formed from isobutane oxidation	-	8.0	16.0	33.3	50.7
Propylene formed from propane oxidation	-	26.4	73.0	185.7	249.6
$\frac{k\ (isobutane)}{k\ (propane)}$	-	5.98	4.48	3.10	3.10

Pressure in Reaction Vessel (mm Hg) x 10^3

Run 43	Initial Mixture	Sample 1	Sample 2	Sample 3	Sample 4
Ethylene	307.4	312.5	310.4	314.8	329.0
Propylene	219.9	339.1	420.9	423.9	544.5
Propylene formed	-	119.2	201.0	204.0	324.6
Isobutene formed	-	245.3	432.4	438.0	662.1
Propylene formed from isobutane oxidation	-	13.3	25.3	25.3	41.1
Propylene formed from Propane oxidation	-	105.9	175.7	178.7	283.5
$\frac{k\ (isobutane)}{k\ (propane)}$	-	2.32	2.46	2.45	2.34

Table 36

Isobutane:Propane:Oxygen = 2:2:1 Pressure = 200 mm Temp = 300°C

Pressure in Reaction Vessel (mm Hg x 10^3)

Sample No.	Isobutene pressure	Propylene formed	Propylene formed from Isobutane	Propylene formed from Propane	$\frac{k(\text{isobutane})}{k(\text{propane})}$
47/1	131.0	65.6	6.9	58.7	2.23
47/2A	350.1	181.0	21.3	159.7	2.19
47/2B	345.7	178.0	21.3	156.7	2.20
47/3A	562.2	292.1	36.7	255.4	2.20
47/3B	550.2	276.4	36.7	239.7	2.29
47/4A	705.5	391.8	49.2	342.6	2.06
47/4B	691.1	337.0	49.2	287.8	2.40
47/5A	862.4	489.8	62.6	427.2	2.02
47/5B	854.9	458.0	62.6	395.4	2.16
47/6	1042.4	596.4	79.3	517.1	2.02
48/1A	189.0	93.1	11.8	81.3	2.33
48/1B	186.6	60.0	11.8	48.2	3.87
48/2A	251.9	89.8	15.7	74.1	3.40
48/2B	256.3	90.2	15.7	74.5	3.44
48/3A	345.0	154.7	21.0	133.7	2.58
48/3B	352.0	141.0	21.0	120.0	2.93
48/4A	524.0	220.3	34.1	186.2	2.81
48/4B	523.3	235.4	34.1	201.3	2.60
48/5A	674.8	311.8	46.5	265.8	2.54
48/5B	677.4	298.4	46.5	251.9	2.69

4. The Initial Stages of Propane Oxidation at 300°C.

Since the product method used in the competitive oxidations depends on isobutene and propylene being equally representative of the consumptions of isobutane and propane, it was necessary to show that the initial conversion of propane at 300°C also resulted in the production of about 80% olefin. Propane oxidation was therefore investigated at low propane conversions. 2:1 Propane;oxygen mixtures at 225 mm pressure were used so that the results could be directly compared to those of isobutane oxidations. As the propane used contained about 1.6% of isobutane, this set of experiments was used as a check on the competitive experiments. The rate constant ratio is given in Table 37 along with the product pressures. Initial product yields in terms of carbon content have been determined as for isobutane oxidations and are illustrated in Figure 46. 80% of the propane consumed is converted to propylene and the minor initial products are acetaldehyde, propylene oxide, propionaldehyde, acetone, methanol and ethanol.

Table 37 (Figure 46)

Propane:Oxygen = 2:1 Pressure = 225 mm Hg Temp = 300°C

Pressure in Reaction Vessel (mm Hg x 10^3)

C_2H_4	C_3H_6	iC_4H_{10}	iC_4H_8	CH_3CHO	$CH_3CH(O)CH_2$	C_2H_5CHO	CH_3COCH_3	CH_3OH	C_2H_5OH	k(isobutane)/k(propane)	Sample No.
63.0	729.0	1172	13.1	132.7	21.3	8.7	26.0	30.0	11.2	2.29	44/1
89.0	1044	1172	21.2	211.6	44.6	17.0	41.7	66.8	19.3	2.60	44/2
134	1276	1172	27.8	277	66.1	23.4	56.1	109.2	23.6	2.79	44/3
107	1496	1172	33.5	320	80.3	25.2	60.7	133	29.4	2.86	44/4
97	1694	1172	40.3	366	101.8	31.2	74.9	166.1	38.0	3.05	44/5
56.1	339	1190	7.6	48.6	10.4	3.2	8.5	51.2	5.1	2.85	45/1
52.6	497	1190	13.5	83.4	16.7	5.6	14.3	67.2	12.8	3.46	45/2
52.6	610	1190	15.7	114.8	22.2	8.6	20.5	55.8	10.8	3.28	45/3
113	1007	1190	20.6	165.5	36.0	12.1	26.8	72.2	14.3	2.61	45/4
73.8	1114	1190	24.6	218.2	46.8	14.9	35.3	92.3	23.1	2.83	45/5
-	526	1185	14.9	104.1	22.0	8.9	20.5	102.1	15.5	3.63	46/1
-	620	1185	16.5	129.5	28.4	11.0	25.6	104.4	19.0	3.39	46/2
-	798	1185	19.8	169.5	35.5	14.0	33.6	112.7	19.7	3.17	46/3
-	885	1185	23.0	199.9	46.1	16.7	37.5	111.2	22.5	3.32	46/4
-	1186	1185	27.7	266	61.8	19.8	47.4	126.8	29.2	3.06	46/5

5. Oxidations in Coated Reaction Vessels.

In order to keep the experimental conditions, other than the reaction vessel surface, as constant as possible, a new reaction vessel of dimensions identical to those of the vessel employed for all earlier oxidations was used. Oxidations were carried out on four different surfaces 1) Boric Acid 2) Hydrogen fluoride washed (silicic acid) 3) Potassium Chloride and 4) Silver.

Boric Acid and H.F. washed surfaces are acidic surfaces on which the rates of reactions are generally increased as the chain propagating HO_2 radical is preserved. Oxidations on these surfaces were carried out at 270°C to ensure a measurable rate of reaction. 2.1 mixtures of isobutane:oxygen were reacted and the results compared to those obtained for similar mixtures in a clean Pyrex vessel. The experimental results are given in Tables 38 and 39 and the comparison graphs in Figures 47-50. Induction periods were considerably shortened and were of the order of three or four minutes instead of four hours. Maximum rates of reaction also increased. That consecutive runs in a Boric Acid coated vessel were not reproducible was probably due to gradual destruction of the Boric Acid coating. Since the results obtained for Boric Acid coated and H.F. treated vessels are extremely similar, these are described together. Generally, the initial yields of oxygenated compounds increase on the acidic surfaces while the initial yields of isobutene are decreased. However, the yields of isobutene oxide and methacrolein are lower than in a clean vessel while that of isobutyraldehyde, which normally behaves in a manner similar to methacrolein yield, increases. The increase in isobutyraldehyde yield is probably due to rapid surface isomerisation of isobutene oxide to isobutyraldehyde [79]. An outstanding feature is the considerable increase in the initial yield of propionaldehyde, particularly as the yield of acetaldehyde is little affected by the nature of the surface. The initial yields of propylene and

acetone also increase, although to a lesser degree than that of propionaldehyde.

Free radicals are destroyed more efficiently on salt surfaces than on acidic surfaces and, hence, oxidations on a Potassium Chloride surface would be expected to proceed more slowly than oxidations in a clean Pyrex vessel. Oxidations in a salt coated vessel were carried out at 300°C and compared to oxidations in a clean vessel under similar conditions. The results are shown in Table 40 and illustrated in Figures 47-50. Little change takes place in the ratio of isobutene yield to minor product total yield but differences do occur in the distribution of minor products. Increases are observed in the yields of isobutyraldehyde and methacrolein. Acetaldehyde yield shows little change but the initial yield of propionaldehyde is halved. The initial yields of acetone, propylene and isobutene oxide show only small variations. These results show that salt surfaces have a different effect on isobutane oxidation from the effect created by acidic surfaces, particularly with respect to the initial yields of propionaldehyde which are greatly increased on acidic surfaces and greatly decreased on salt surfaces.

Metal surfaces are extremely efficient radical destroyers and it was thought that the oxidation of a 2:1 isobutane:oxygen mixture at 300°C on a silver surface would be completely inhibited. This inhibition did not occur as the oxidation commenced at the maximum rate of reaction. Autocatalysis was not observed, indicating that the reaction was no longer a degenerate branching reaction. Analysis by flame ionisation detection showed that only minor amounts of products typical of isobutane oxidation were being produced. Isobutene and very small amounts of two other butenes, probably 1- and 2- butenes formed by catalytic isomerisation, were found together with small amounts of propylene and ethylene. Oxygenated compounds detected were isobutene oxide and the unidentified product, X, which was thought to be 3-methyl oxetane. No aldehydes other than

a very small amount of isobutyraldehydewere detected. This small yield was probably formed by isomerisation of isobutene oxide. As the pressures of these products could not account for the observed pressure rise in the reaction vessel, katharometer detection was applied in addition to flame ionisation detection and the yields of carbon oxides examined. Large yields of carbon dioxide were found. These results were compared by means of a product pressure / ΔP curve to the results of similar oxidations in a clean vessel. Results given in Table 41 are compared in Figure 51. Isobutene yield in the silver vessel is one-tenth of that in the clean vessel while the pressure of carbon dioxide in the silver vessel is about six times that in a clean vessel. This evidence strongly suggests that carbon dioxide is formed as a result of a heterogeneous process.

Studies of oxidations on different surfaces, summarised in Table 42, have shown that the distribution of the initial product yields is dependent on the nature of the reaction vessel surface.

Table 38 (Figures 47-50)

isoButane:Oxygen = 2:1

Boric Acid coated Reaction Vessel.

Pressure = 225 mm Hg

Temp = 270°C

Pressure in Reaction Vessel (mm Hg x 10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_3CH(O)CH_2$	$(CH_3)_2C(O)CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	CH_3OH	X	Sample No.
369	1.9	25.8	9.4	0.4	0.5	50.5	18.3	29.2	1.7	54.8	6.5	65/1
732	3.7	44.8	25.4	1.2	2.6	115.9	47.6	68.1	3.2	51.1	-	65/2
1081	7.0	85.5	53.6	2.2	4.5	198	83.3	135	6.3	106	27.5	65/3
1690	15.6	179	111.3	5.0	11.4	326	149	281	8.9	191	33.9	65/4
2471	32.9	333	234	13.1	30.0	510	262	596	19.6	411	84.9	65/5
999	6.8	76.0	45.6	2.4	8.9	160	65	144	4.8	147	63.8	66/1
1353	10.9	121	71.4	3.6	14.7	229	94	191	7.4	204	87.0	66/2
1739	16.3	177	115.0	6.2	28.1	326	137	305	10.4	278	107.2	66/3
2327	25.1	271	190.3	10.7	55.3	421	177	487	17.3	362	138	66/4
2922	44.5	433	280	15.9	88.9	536	233	739	25.0	464	171	66/5

Table 39 (Figures 47-50)

isoButane:Oxygen = 2:1 Pressure = 225 mm Hg Temp = 270°C

Reaction vessel washed with Hydrofluoric acid.

Pressure in reaction vessel (mm Hg x 10^3)

iC_4H_8	C_3H_6	C_2H_4	CH_3CHO	$CH_3CH(O)CH_2$	$(CH_3)_2C(O)CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	CH_3OH	X	Sample No.
642	37.7	3.0	21.8	1.5	3.7	105	34.7	60.8	2.2	41.3	28.5	69/1
1009	79.3	5.9	46.0	2.7	10.9	180	64.8	118	4.5	71.6	45.4	69/2
1543	149	12.4	101	5.3	23.7	312	118.2	254	9.3	187.3	77.6	69/3
2155	260	26.3	167	7.7	21.5	405	171	407	12.7	301	84.9	69/4
2905	441	45.2	284	16.8	36.7	562	264	749	23.2	413	139.2	69/5
1850	162	22.8	-	-	-	-	-	-	-	-	-	70/2
2199	205	28.2	119	9.9	70.3	348	128.5	313	14.6	223	119.5	70/3
2618	282	41.4	173	13.5	106.6	435	163	439	20.2	293	147.2	70/4
3219	380	60.6	222	18.8	125	486	191	585	25.9	381	142.6	70/5

Table 40 (Figures 47-50)

isoButane:Oxygen = 2:1 Pressure = 225 mm Hg Temp = 300°C

Potassium chloride coated reaction vessel.

Pressure in Reaction vessel (mm Hg x 10^3)

iC_4H_8	C_2H_4	C_3H_6	CH_3CHO	$CH_3CH(O)CH_2$	$(CH_3)_2C(O)CH_2$	C_2H_5CHO	I.B.A.	CH_3COCH_3	M.A.	CH_3OH	X	Sample No.
208	1.8	9.3	19.8	2.6	14.6	10.0	6.2	18.0	2.9	24.5	3.2	67/1
489	1.8	18.6	32.5	5.4	20.2	15.3	15.1	27.4	4.2	17.4	9.1	67/2
638	2.3	23.5	44.1	8.2	25.8	20.6	24.1	42.7	6.7	43.7	15.3	67/3
825	3.3	30.4	60.4	12.4	30.7	27.1	36.4	63.5	9.2	39.1	17.5	67/4
1020	3.7	38.9	69.7	15.7	22.5	30.5	52.7	69.9	10.9	36.3	22.1	67/5
416	1.5	14.5	23.6	4.5	11.0	15.8	14.3	24.6	3.8	17.2	6.3	68/1
749	2.6	26.0	51.5	10.3	24.9	27.6	29.7	53.4	7.5	26.0	16.1	68/2
931	3.4	34.0	65.5	14.5	33.3	29.0	35.3	86.3	13.2	34.0	22.6	68/3
1111	4.4	42.1	80.4	17.6	32.8	29.4	41.6	128.9	17.6	46.5	28.7	68/4
1297	5.0	50.7	91.4	20.6	51.1	28.0	39.6	164.0	23.0	28.2	36.2	68/5

Table 41 (Figure 51).

isoButane:Oxygen = 2:1 Pressure = 225 mm Hg Temp = 300°C

Silver coated reaction vessel.

Pressure in Reaction Vessel (mm Hg)

Oxygen	79.7	69.3	69.1	67.6	57.9
Carbon Monoxide	0.00	0.08	0.09	0.12	0.13
Ethylene	0.008	0.016	0.030	0.044	0.077
Propylene	0.006	0.015	0.022	0.029	0.036
Carbon Dioxide	1.50	2.94	4.85	8.23	11.13
Isobutane	148.2	146.5	136.4	140.9	139.7
Isobutene	0.343	0.657	0.804	0.789	0.655
Butene -1	-	0.013	0.018	0.023	0.029
Butene -2	-	0.012	0.018	-	0.022
Propylene Oxide	0.001	0.001	0.002	0.003	0.004
Isobutyraldehyde	0.003	0.002	0.003	0.003	0.003
Acetone	0.003	0.006	0.004	0.007	0.004
X	0.027	0.087	0.115	0.141	0.127
Isobutene Oxide	0.028	0.012	0.013	0.010	0.006
ΔP (mm)	1.329	1.994	2.557	3.333	4.360

Table 42 (Figures 47-50)

Variation of initial product yield with Reaction Vessel Surfaces.

Isobutane = 150 mm, Oxygen = 75 mm

Temp °C	300	300	300	270	270	270	270
Runs Nos.	28-31	67	68	49-52	65	66	69
Surface	C.P.	K.Cl	K.Cl	C.P.	B.A.	B.A.	H.F.
Key letter	A	B	C	D	E	F	G
Initial Yields							
Isobutene	0.80	0.83	0.80	0.80	0.74	0.68	0.71
Isobutene Ox.	0.045	0.050	0.025	0.008	0.003	0.006	0.006
Acetone	0.027	0.042	0.036	0.056	0.052	0.067	0.053
Propylene	0.034	0.022	0.021	0.021	0.031	0.037	0.036
Acetaldehyde	0.026	0.028	0.026	0.018	0.014	0.015	0.013
Propionaldehyde	0.044	0.018	0.019	0.034	0.087	0.080	0.085
Isobutyraldehyde	0.018	0.030	0.030	0.028	0.041	0.044	0.042
Methacrolein	0.007	0.010	0.011	0.010	0.004	0.003	0.004

C.P. = Clean Pyrex B.A. = Boric Acid H.F. = Hydrogen Fluoride washed.

Discussion

1. The slow oxidation of Isobutane

In addition to consideration of the modes of primary product formation, this section includes discussion of product formation in the later stages of the oxidation in which co-oxidation of isobutane and its primary oxidation products occurs. Reaction mechanisms for product formation are considered and the dependence of the initial product yields on temperature and mixture composition is discussed. In some cases, the relative amounts of products formed can be explained. The thermal data used for evaluating changes in heat content in the reactions invoked in this section is given along with the source of the data.

Thermal Data

The enthalpy changes occurring in the reactions listed in this section have been calculated from the heats of formation of products and reactants. Although the free energy change is the factor which determines the possibility of a reaction occurring, the enthalpy is more easily obtained and can be used as a guide to the feasibility of a reaction. However, the factor which determines which of a number of possible reactions will take place is neither the free energy nor the enthalpy but the activation energy as the activation energy determines the rate of the reaction. Polanyi [80] has demonstrated that, for the reaction of Na with alkyl halides, the activation energy of the reaction is proportional to the exothermicity of the reaction, i.e. the greater the exothermicity, the lower the activation energy. Although Polanyi's relation does not apply to other reactions, the endothermicity of a reaction does give an idea of the possibility of the reaction occurring. When a number of reactions are possible, the most exothermic is preferred.

The heat data given in the table below have, unless otherwise indicated, been taken from the following sources.

Heats of Formation of Molecules - "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds" - Rossini et al. or "Circular 500 Selected Values of Chemical Thermodynamic Properties, 1952".

Heat of Formation of Radicals - "Gas Kinetics" by A.F. Trotman-Dickenson.

Heat of Formation of H_2O_2,HO_2 - Foner and Hudson, J. Chem. Phys. 1955, 23, 1364.

Table 43

Molecule	ΔH_f (25°C) k cal/mole	Radical or Atom	ΔH_f (25°C) k cal/mole
Ethane	-20.2	t-butyl [83]	6
Ethylene	12.5	Br	26.7
Propylene	4.9	H	52.0
Isobutane	-32.1	CH_3O	-1.0
Isobutene	-4.0	ethyl	25.2
Methane	-17.9	n-propyl	22.0
Carbon Monoxide	-26.4	sec-butyl *	14.0
Carbon Dioxide	-94.0	OH	10.1
Water	-57.8	HO_2	5
Hydrogen Peroxide	-31.8	iso-propyl	17
Acetaldehyde	-39.8	ethoxy	-8
Propionaldehyde [81]	-46.0	methyl	32.5
n-Butyraldehyde [81]	-52.5	CHO	6
Acetone [82]	-51.8	isobutoxy [21]	-18
Methanol	-48.1	t-butoxy [21]	-25
Ethanol	-57.0		
Formaldehyde	-27.7		
Hydrogen Bromide	-8.7		

*Calculated from ΔH of $iC_4H_{10} = iC_4H_9 + H$

Mechanism of the Oxidation

In the introduction, stress was laid on the fact that many of the investigations carried out by early workers on hydrocarbon oxidation resulted in accumulation of information about the later stages of these oxidations. Such results were inevitable as the comparatively insensitive analytical methods of that time were used and large amounts of products were necessary for analysis. In the later stages of alkane oxidations, the concentration of olefin reaches about 10% of that of the parent alkane and, since olefins oxidise at a greater rate than alkanes, the olefin and alkane are being consumed at about the same rates in the later stages of the oxidation. Consequently, the products determined in much early work were the result of co-oxidation of olefin and alkane. In order to distinguish between products which arise from isobutane oxidation and those of isobutene oxidation, isobutene oxidation in the temperature range 250-350°C has been undertaken concurrently in this laboratory [79]. This discussion is divided into two sections a) the initial stages and b) the later stages in which the part played by the oxidation of olefins and oxygenated compounds is considered.

a) Initial stages of the oxidation

Both the low conversion studies and the overall oxidation show that the initial products of isobutane oxidation are isobutene, propylene, carbon monoxide, carbon dioxide, ethylene, acetaldehyde, propylene oxide, isobutene oxide, propionaldehyde, isobutyraldehyde, acetone, methacrolein and methanol. Isobutene is the major initial product and accounts for 75-80% of the isobutane consumed. It is generally agreed that the initiation process of alkane oxidation results in the formation of an alkyl radical and an HO_2 radical and that these radicals take part in the chain propagating steps.

Consider the possible fates of an alkyl radical as outlined in the hypothetical scheme below.

1) $R + O_2 \xrightarrow{k_1}$ Product A + radical.

2) $R \xrightarrow{k_2}$ Product B + R'

3) $R + O_2 \xrightarrow{k_3} X$ + Product

$X + O_2 \xrightarrow{k_4}$ Product C

The relative yields of A and B are given by the equation

$$\frac{\text{Yield of A}}{\text{Yield of B}} = \frac{k_1 [R] [O_2]}{k_2 [R]} = k [O_2]$$

The yield of A relative to B would increase with increase in oxygen pressure.

Similarly, $$\frac{\text{Yield of C}}{\text{Yield of A}} = \frac{k_4 [O_2]\, k_3 [R] [O_2]}{k_1 [R] [O_2]} = k' [O_2]$$

The relative yields of C and B show a dependence on the square of the oxygen pressure.

i.e. $$\frac{\text{Yield of C}}{\text{Yield of B}} = \frac{k_4 [O_2]\, k_3 [R] [O_2]}{k_2 [R]} = k'' [O_2]^2$$

Thus, competing reactions of the type shown above result in the relative product yields having a strong dependence on oxygen pressure.

In the present work on isobutane oxidation, comparison of the relative yields of primary products over an eighteen fold change in hydrocarbon.: oxygen ratio shows that the initial yields of products do not depend on hydrocarbon : oxygen ratio. No product ratio altered by more than a factor of two although the oxygen pressure was varied by a factor of six (from 20 mm to 133 mm). Thus, all product forming reactions have the same dependence on oxygen i.e. an alkyl radical reacts with oxygen to form products.

One mode of attack of oxygen on t- and iso-butyl radicals results in the formation of isobutene and HO_2. Chain propagation occurs by HO_2 attack on isobutane to form iso- and t-butyl radicals. Although the results of competitive alkane oxidations have suggested that HO_2 may not be the radical attacking the hydrocarbon, evidence will be put forward in a later section that, in the initial stages of alkane oxidation, HO_2 does attack the alkane. The major process of the initial stages of isobutane oxidation between 270 and 330°C can be represented by an HO_2 radical chain resulting in the formation of isobutene and hydrogen peroxide.

i.e. $tC_4H_9 + O_2 \longrightarrow iC_4H_8 + HO_2$ (1) $\Delta H = -5$ k cal.

$iC_4H_{10} + HO_2 \longrightarrow tC_4H_9 + H_2O_2$ (2) $\Delta H = +1$ k cal.

$iC_4H_9 + O_2 \longrightarrow iC_4H_8 + HO_2$ (3) $\Delta H = -13$ k cal.

$iC_4H_{10} + HO_2 \longrightarrow iC_4H_9 + H_2O_2$ (4) $\Delta H = +9$ k cal.

Although the reactions involving HO_2 attack on iC_4H_{10} are endothermic, the overall processes forming isobutene from isobutane are exothermic. Since the activation energies of (2) and (4) are likely to be about 5 k cal. greater than their endothermicities, reaction (2) involving the formation of t-butyl radicals

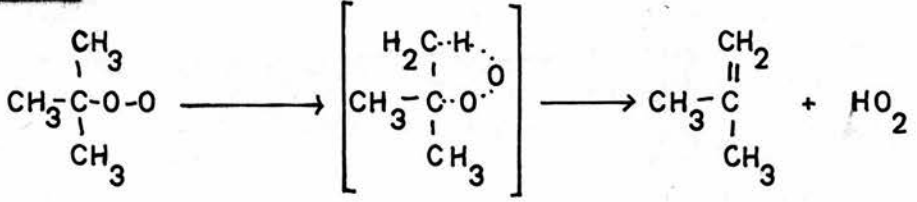
has a considerably lower activation energy than that,(4), forming isobutyl radicals. The concentration of t-butyl radicals is likely to be greater than that of isobutyl radicals despite the numerical superiority of primary H atoms in isobutane.

However, oxygen may also add to alkyl radicals to form alkyl peroxy radicals. The addition of an alkyl radical to oxygen is an exothermic process and the alkyl peroxy radicals carry away the energy of collision. Butyl peroxy radicals are likely to be able to undergo a large number of collisions before losing this excess vibrational energy as it is distributed over a large number of degrees of freedom. These butyl peroxy radicals may undergo intramolecular decomposition to form oxygenated products.

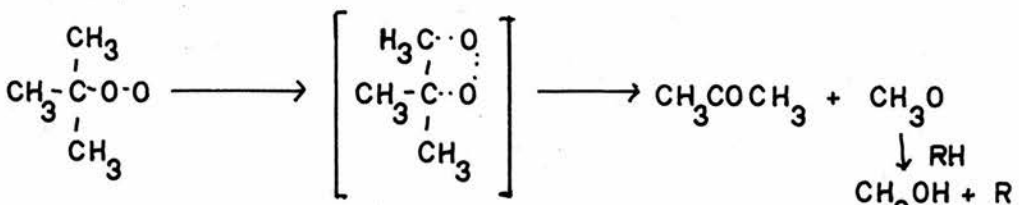
Zeelenberg [52] has proposed that all the products of isobutane oxidation at 300°C result from the intramolecular decomposition of iso-butyl peroxy and t-butyl peroxy radicals. This scheme is outlined below and the likely transition state involved in the formation of each product is given in square brackets.

1.) Products arising from t-butyl peroxy radicals.

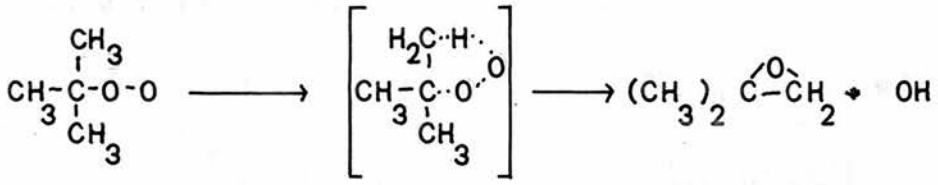
a) Isobutene



b) Acetone and Methanol

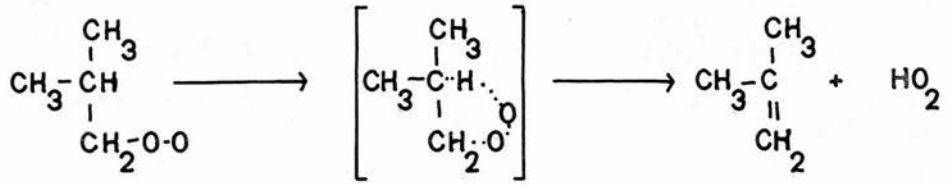


c) Isobutene Oxide

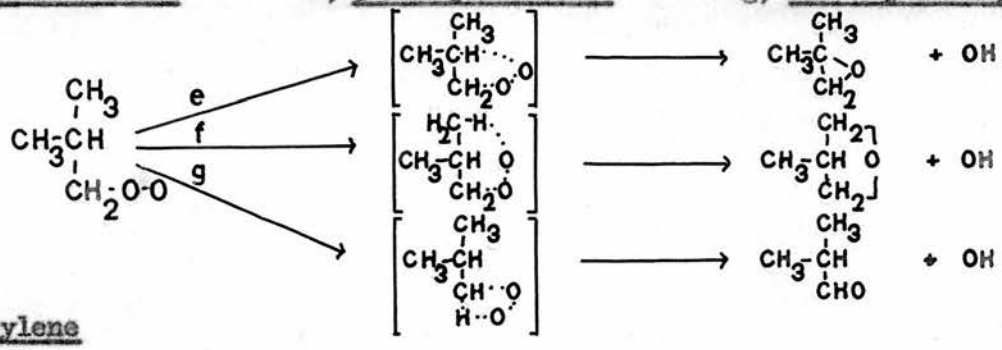


2. Products from iso-butyl peroxy radicals

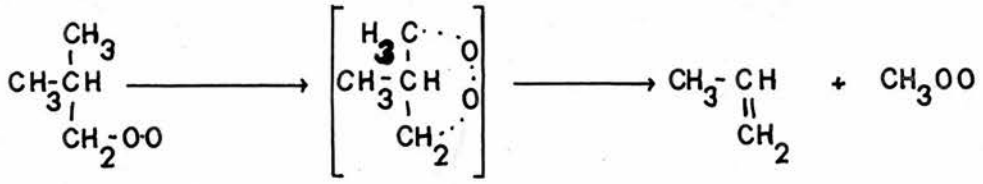
d) Isobutene



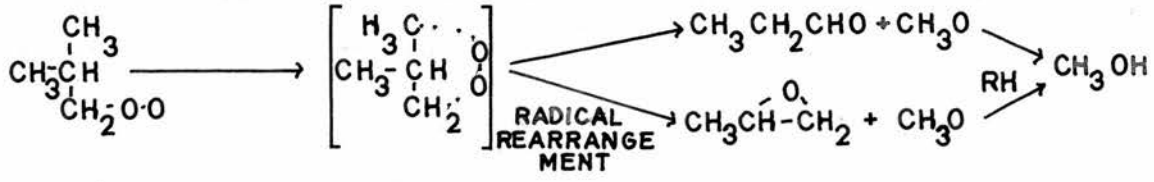
e) Isobutene Oxide f) 3 methyl Oxetane g) Isobutyraldehyde



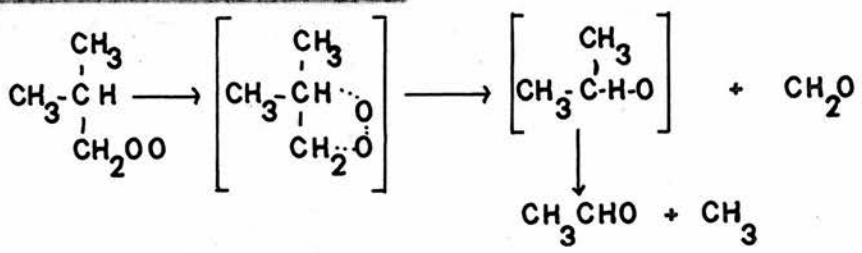
h) Propylene



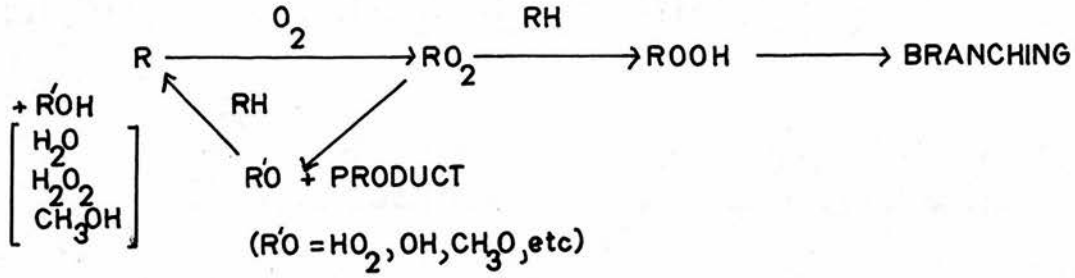
i) Propionaldehyde, Propylene Oxide and Methanol



j) Acetaldehyde and Formaldehyde



This scheme can be represented in a general cyclic form



These intramolecular decompositions all involve two bond breaking and two bond making processes before product formation occurs. Each decomposition can for sake of clarity be thought of as occurring in two stages. The bonds broken in each stage are outlined below together with the overall enthalpy change of the reaction producing each product from the appropriate butyl peroxy radical. Bonds strengths used in these calculations are as follows:-

primary CH ~ 98 k cal, C-C ~ 85 k cal., C-O ~ 90 k cal., C=O ~70 k cal., C=C ~75 k cal., tert C-H ~90 k cal., O-H ~90 k cal., O-O ~45 k. cal.

?

~70 kcal to account for ΔH's in table overleaf.

Product	Bond Broken	Bond Formed	Bond Broken	Bond Formed	ΔH k cal.
1) from t-butyl peroxy					
a) Isobutene	C-H	O-H	C-O	C=C	+28
b) Acetone	C-C	C-O	O-O	C=O	-35
c) Isobutene Oxide	C-H	O-H	O-O	C-O	-37
2) from iso-butyl peroxy					
d) Isobutene	C-H	O-H	C-O	C=C	+20
e) Isobutene Oxide	O-H	O-H	O-O	C-O	-45
f) 3 methyl Oxetane	C-H	O-H	O-O	C-O	-37
g) Isobutyraldehyde	C-H	O-H	O-O	C=O	-22
h) Propylene	C-C	C-O	C-O	C=C	+15
i) Propionaldehyde	C-C	C-O	O-O	C=O	-30
Propylene Oxide	C-C	C-O	O-O	C-O	-50
j) Formaldehyde	C-C	O-H	O-O	C=O	-30
Acetaldehyde	C-C	O-H	C-C	C=O	-60
			O-O	C=O	

From the above table, it is clear that the reactions forming oxygenated compounds from butyl peroxy radicals are exothermic while those producing isobutene and propylene are endothermic to the extent of 15-20 k cal. The reactions forming isobutene would be expected to have considerably higher activation energies than those reactions forming oxygenated compounds and would be expected to take place more slowly since, as all the transition states involved are of similar structure, the A factors for all intramolecular decompositions will be similar. The experimental results of the present work show that isobutene is the major product and that the A factor for the reaction forming isobutene is

10^3 - 10^4 times greater than that of the reaction forming acetone. These results are in agreement with the idea that isobutene is formed by direct abstraction of H from butyl radicals by oxygen while acetone is formed as a result of butyl peroxy radical decomposition, the latter process involving a low entropy transition state. The experimental evidence leads to the conclusion that only isobutene is formed as a result of direct H abstraction while all oxygenated compounds are formed by intramolecular decompositions of butyl peroxy radicals.

Zeelenberg's scheme can account for the formation of most of the minor products by decomposition reactions of butyl peroxy radicals which involve not unreasonable transition states. The cyclic scheme illustrated earlier does not result in a pressure increase in the system and, although such a scheme may hold in the very early stages of the oxidation when product formation is occurring although no pressure increase is taking place, additional reactions must be introduced to account for the pressure rise. This scheme also fails to account for the formation of methacrolein and ethylene both of which are initial, though minor, products of isobutane oxidation. Zeelenberg states that methacrolein originates from oxidation of the main primary product, isobutene, but the yield of methacrolein obtained from isobutene oxidation [79] is too low to account for the formation of methacrolein in isobutane oxidation by oxidation of isobutene. Zeelenberg also postulates that the initial yields of methanol and acetone are equal (reaction b) in his scheme). This is extremely unlikely as, except at low oxygen concentrations, methoxy radicals are much more likely to undergo oxidation than to abstract H to form methanol. As the oxygen pressure increases, an increase in the yields of aldehydes, acetaldehyde and propionaldehyde, relative to acetone occurs. This increase in aldehyde yields in oxygen rich mixtures is thought by Zeelenberg to be due to variations in the relative concentrations of t-butyl and iso-butyl radicals. In oxygen deficient mixtures, iso-butyl radicals may abstract from

isobutane to form t-butyl radicals which are thermodynamically more stable.

$$iC_4H_9 + iC_4H_{10} = t\text{-}C_4H_9 + iC_4H_{10}$$

Since aldehydes can arise only from reactions of iso-butyl peroxy radicals, the yields of aldehydes relative to acetone are reduced in oxygen weak mixtures.

A scheme such as Zeelenberg's should result in a slow unidirectional trend in product distribution with increase in temperature. Product distribution should be independent of mixture composition as all products start from butyl peroxy radicals.

The present experiments show that as the reaction temperature falls the yield of acetone relative to isobutene increases while the yield of propylene relative to isobutene falls. These features can be explained qualitatively by consideration of the enthalpies of the reactions forming the respective products.

e.g. for acetone and isobutene - both products may be thought of as arising from the reaction of a t-butyl radical with oxygen although acetone formation must take place through a butyl peroxy radical.

$$tC_4H_9 + O_2 = iC_4H_8 + HO_2 \qquad (1)\ \Delta H = -5 \text{ k cal.}$$

$$tC_4H_9 + O_2 = CH_3COCH_3 + CH_3O \qquad (5)\ \Delta H = -59 \text{ k cal.}$$

Reaction (5) being the more exothermic will be favoured at lower temperatures and the yield of acetone may be expected to rise relative to that of isobutene at lower temperatures.

Similarly, the reactions forming propylene are:

$$iC_4H_9 + O_2 = iC_4H_8 + HO_2 \qquad (3)\ \Delta H = -13 \text{ k cal.}$$

$$iC_4H_9 + O_2 = CH_3CH=CH_2 + CH_3OO \qquad (6)\ \Delta H = +10 \text{ k cal.}$$

At higher temperatures, reaction (6) forming propylene is favoured relative to reaction (3) as reaction (6) has the higher endothermicity and hence the higher activation energy.

These temperature dependences have been verified experimentally in both sets of experiments which have been carried out. Although activation energy differences could not be calculated with great accuracy as oxidations were carried out at only three temperatures, the experimental results indicate that the activation energy difference between reaction (3) and reaction (6) is 8 k cal. Studies using katharometer detection yielded 8 ± 0.5 k cal. and studies using flame ionisation detection gave 11 ± 2 k cal. for the activation energy difference of reactions (1) and (5). Knox and Wells [51] have proposed that in the oxidation of ethane at temperatures between 320 and 380°C an equilibrium exists between ethyl and ethyl peroxy radicals. This equilibrium has been proposed to account for the dependence of the ethylene/formaldehyde ratio on temperature. Ethylene is formed by direct abstraction of H from ethyl by oxygen while formaldehyde results from the decomposition of an ethyl peroxy radical. The essential equations for this scheme may be written as:

$$C_2H_5 + O_2 \xrightarrow{(A)} C_2H_4 + HO_2$$

$$C_2H_5 + O_2 \overset{(B)}{\rightleftharpoons} C_2H_5OO$$

$$C_2H_5OO \xrightarrow{(D)} CH_2O + CH_3O$$

The temperature dependences of acetone/isobutene and isobutene/propylene ratios in isobutane oxidation at temperatures around 300°C may be represented by a similar scheme.

i.e. $C_4H_8 + HO_2 \xleftarrow{(1)} tC_4H_9 + O_2 \underset{(-7)}{\overset{(7)}{\rightleftharpoons}} tC_4H_9OO \xrightarrow{(8)} CH_3COCH_3 + CH_3O$

and $C_4H_8 + HO_2 \xleftarrow{(3)} iC_4H_9 + O_2 \underset{(-7')}{\overset{(7')}{\rightleftharpoons}} iC_4H_9OO \xrightarrow{(8')} CH_3CH = CH_2 + CH_3OO$

Provided that the equilibria are not upset by reactions (1), (3), (8) and (8'), then the apparent activation energy differences and A factor ratios are

$$E_1 - E_5 = E_1 - \Delta H_7 - E_8. \quad A_1/A_5 = A_1 \exp [-\Delta S_7/R] /A_8$$

and $E_3 - E_6 = E_3 - \Delta H_7 - E_{8'}. \quad A_3/A_6 = A_3 \exp [-\Delta S_7/R] /A_{8'}$

ΔH_7 may be estimated from the $(R-O_2)$ bond strength. The only well established peroxy bond strength is that of HO_2 [73] $D(H-O_2) = 45$ k cal. An estimate of the maximum bond strength $D(R-O_2)$ may be made on the basis of the reactions of alkyl peroxy radicals and thermochemical data on alkyl and alkoxy radicals. CH_3OO [84], C_2H_5OO [85] and C_4H_9OO [86] radicals disproportionate at room temperature and the disproportionation reactions are unlikely to be endothermic. On the assumption that the reaction

$$2RO_2 \longrightarrow 2RO + O_2$$

is thermoneutral, a minimum value of ΔH_f, (RO_2) can be obtained using known data for alkoxy radicals. From the reaction

$$RO_2 \longrightarrow R + O_2$$

the maximum bond strength $D(R-O_2)$ may be calculated using known thermochemical data for alkyl radicals. Such calculations have been made for R = CH_3, C_2H_5, iC_4H_9 and tC_4H_9. The maximum bond strength $D(R-O_2)$ is 30 k cal. A value of $\Delta H_7 = -25$ k cal. is therefore reasonable. The direct abstraction reactions (1) and (3) are exothermic and probably have low activation energies (~5 k cals.)

The peroxy radical decomposition (8) must for decomposition into significant products have an activation energy greater than the (R-OO) bond strength i.e. greater than 25 k cal. Thus, the maximum activation energy difference $E_1 - E_5$ is about 5 k cal. The peroxy radical decomposition (8') is endothermic (+15 k cal.) and the activation energy may be about 15 k cal. greater than that of (8). The activation energy difference between (3) and (6) is therefore about 10 k cal. The overall activation energy differences found experimentally are therefore possible on the basis of this equilibrium.

A butyl/butyl peroxy radical equilibrium is not able to explain the variation of the relative amounts of isobutene and minor oxygenated products with mixture composition variation. (Figure 15). From the above equilibrium scheme, the rate of formation of isobutene relative to acetone is given by the equation

$$\frac{\text{Rate of formation of isobutene}}{\text{Rate of formation of acetone}} = \frac{k_1 [tC_4H_9] [O_2]}{k_8 [tC_4H_9O_2]} = \frac{k_1}{k_8 K}$$

where K is the equilibrium constant. K is constant at constant temperature and thus the relative yields of minor and major products should be independent of mixture composition.

As temperature rises, K decreases as the rate of decomposition of RO_2 will increase relative to the rate of its formation. Thus, the rate of isobutene formation relative to acetone formation should be greater at higher temperatures.

Knox and Wells [51] have calculated the entropy loss on formation of the ethyl peroxy radical from ethyl and oxygen (reaction B) to be 32 cal/deg. mole. They have also estimated the entropy loss in forming the transition state in the reaction forming formaldehyde from ethyl peroxy (reaction D). Use of the experimental ethylene/formaldehyde ratio and these entropy changes has

enabled the maximum activation energy difference between the reactions forming ethylene and formaldehyde to be calculated. This value of 25 k cal. is less than the experimental value of 35 k cal. If the equilibrium is not upset by decomposition of ethyl peroxy to formaldehyde, reaction (D) must be at least 10 times slower than (C). Thus, the A factor of (C) is $10^{17.5}$ which is unacceptably high and is not consistent with the entropy loss in (D). These discrepancies show that the temperature dependence of the formaldehyde/ethylene ratio is not fully explained. Similar inconsistencies exist when butyl peroxy radical reactions are considered.

The initial yield of formaldehyde has been shown to be considerably higher than that of any other oxygenated product (Figures 6 and 11). As every C_3 product formed must result in the formation of a C_1 fragment, it is not surprising that the initial yield of formaldehyde is greater than that of each individual C_3 product. Consideration of Zeelenberg's scheme for the formation of the minor products shows that, in addition to the formation of formaldehyde in reaction j), C_1 radicals are also formed in reactions b), h), i), and j), in which acetone, propylene, propylene oxide and propionaldehyde, and acetaldehyde are formed respectively. If CH_3, CH_3O and CH_3OO radicals are all converted to formaldehyde, the initial pressure of formaldehyde would be equal to the sum of the pressures of acetone, propylene, propionaldehyde, propylene oxide and acetaldehyde. The actual formaldehyde pressure is about 80% at 300°C and 60% at 330°C of the sum of the C_3 product pressures. This may be due to methyl and methoxy radicals abstracting from good H donors to form methane and methanol. The normal reactions of methyl and methoxy are oxidation to form formaldehyde.

i.e. $CH_3 + O_2 = CH_2O + OH$ (9) $\Delta H = -50$ k cal.

$CH_3 + iC_4H_{10} = CH_4 + tC_4H_9$ (10) $\Delta H = -12$ k cal.

$CH_3O + O_2 = CH_2O + HO_2$ (11) $\Delta H = -22$ k cal.

$CH_3O + iC_4H_{10} = tC_4H_9 + CH_3OH$ (12) $\Delta H = -9$ k cal.

As the reactions producing formaldehyde are more exothermic than those producing methane or methanol, these are the preferred reactions at low temperatures. Methane is not produced untilthe oxygen is almost exhausted and the initial yield of methanol is low. Reactions (10) and (12) are not important in the early stages of isobutane oxidation at 300°C.

Formaldehyde is also formed by decomposition of the methyl peroxy radical

i.e. $CH_3OO \rightarrow CH_2O + OH$ (13) $\Delta H = -37$ k cal.

The curvature in the formaldehyde/ΔP curves (Figures 6 and 11) as ΔP increases can be attributed to increasing importance of abstraction by methyl and methoxy and degradation of formaldehyde.

$CH_2O + HO_2 = CHO + H_2O_2$ (14) $\Delta H = -3$ k cal.

$CHO + O_2 = CO + HO_2$ (15) $\Delta H = -27$ k cal.

As formaldehyde is produced both by the decomposition of an isobutyl peroxy radical and the oxidation of other radicals which are produced from butyl peroxy radical decomposition, the decrease in formaldehyde yield relative to isobutene with increase in temperature can be explained by the decrease in the concentration of butyl peroxy radicals relative to butyl radicals. At the higher temperatures, abstraction reactions of methoxy etc. increase in importance relative to oxidation reactions.

Plots of log (product pressure) against time have indicated that product development is exponential with time. Figures 28A and 28B show that for the later stages of the reaction, which are certainly not diffusion controlled as inert gas has no effect on the maximum rate, product development parallels increase in pressure rise. Figures 41 and 42 indicate that products are also produced exponentially with time during the initial stages of the induction period. Pressure increase under the conditions described in Figure 41 commences after four hours. The lines of Figure 41 represent the product development after a reaction time of about two hours when no increase in pressure has been observed. Figure 28A and 28B show that, in the middle stages of the acceleration where the straight line portion of the $d\Delta P/dt$ against ΔP curve occurs, product formation is occurring exponentially and that the branching factors for all products with the exception of isobutene oxide are roughly constant. This result is consistent with the idea that the products are formed from butylperoxy radicals, the concentration of which increases exponentially. The results of Figure 41 are of particular interest as the exponential development indicates that branching is occurring during the induction period although product formation does not produce a pressure rise. This conclusion contrasts with that of Knox [87]. Knox showed that the rate/pressure rise curve in propane oxidation had an initial period of slow oxidation which was thought to be a build up period before exponential acceleration took place. Thus, in isobutane oxidation, the pressure rise is not a strictly reliable measure of the extent of reaction in the very early stages. The branching factors of secondary products produced by radical attack on primary products would be twice these of primary products. Primary

product and radical concentrations increase according to the equation $C = C_o e^{\phi t}$. Thus, a secondary product is formed according to the equation

$$\text{Rate of formation} = C_o e^{t} \cdot C_1 e^{\phi t} = k e^{2\phi t}$$

The branching factor in this case is 2ϕ. The only possible secondary product is isobutene oxide as its branching factor is about twice that of all other products (Figure 41). Isobutene oxide may result from HO_2 attack on isobutene and consequent breakdown to form OH and isobutene oxide.

$$(CH_3)_2 C = CH_2 + HO_2 \longrightarrow CH_3C\text{-}CH_2OOH \longrightarrow (CH_3)_2\overset{\bullet}{C}\text{-}CH_2 + OH$$

The conclusion that, as a result of this difference in ϕ, isobutene oxide is a secondary product must be treated with reserve as, since isobutene is not the major product of HO_2 radical attack on isobutene [79], ϕ acetone and ϕ isobutene oxide would be expected to show a similar variation in branching factor when compared to ϕ for propionaldehyde which is not a product of isobutene oxidation. Zeelenberg [51] states that CO_2 has a branching factor 2ϕ, a result which has not been observed in this work. It is noticeable, however, from Figure 28B that, near the end of the reaction, the branching factors of ΔP and acetone are increasing. This increase supports the view that the pressure rise takes place as a result of secondary oxidation processes.

The main conclusions reached on the initial stages of isobutane oxidation are as follows.

1) Product forming reactions all have the same dependence on oxygen.

2) Isobutene is formed by direct abstraction of H by O_2 from butyl radicals whereas oxygenated compounds are formed by decomposition reactions of butyl peroxy radicals.

3) The temperature variations of the ratios of the initial yields of acetone/isobutene and propylene/isobutene can only be partly explained by the equilibrium

$$C_4H_9 + O_2 \rightleftharpoons C_4H_9O_2$$

4) No simple mechanism exists for the dependence of the initial product yields on hydrocarbon/oxygen ratio.

5) Branching reactions occur during the induction period although no pressure rise occurs.

6) Examination of Figures 52 and 53 shows that the effects of temperature and mixture composition variations cannot be interpreted on the basis of a simple peroxy radical scheme as envisaged by Zeelenberg.

b) <u>Later stages of the oxidation</u>.

In the later stages of the oxidation, the major products are water, oxides of carbon, acetone and isobutene. Increases are observed in the yields of methanol and methane. In all mixtures studied, the yields of propionaldehyde passed through a maximum while those of acetaldehyde flattened off. In the oxygen rich mixture studied (isobutane:oxygen = 1:2), the isobutene pressure passed through a maximum indicating that isobutene was being consumed faster than it was being formed. The effects of isobutene co-oxidation are not easily distinguished as the products of the two oxidations are so similar. All the oxygenated compounds formed in isobutane oxidation, with the exception of propionaldehyde, are also formed in isobutene oxidation at 300°C. A late rise in acetone and isobutene oxide yields is certainly due to isobutene oxidation.

Water arises from two reactions. Abstraction reactions of OH with either the parent alkane or oxidation products give water.

$$OH + RH \longrightarrow H_2O + R \qquad (16)$$

Water also occurs from the heterogeneous decomposition of hydrogen peroxide to an extent dependent on the ability of the reaction vessel to decompose peroxides. In the present reaction vessel, heterogeneous decomposition of hydrogen peroxide occurs to a large extent.

The source of methanol has always been an important problem in hydrocarbon oxidation. It is generally supposed to arise from the reaction

$$CH_3O + RH = CH_3OH + R \qquad (12)$$

Methoxy radicals are, however, usually oxidised to formaldehyde and HO_2

$$CH_3O + O_2 = CH_2O + HO_2 \qquad (11)\ \Delta H = -22 \text{ k cal.}$$

Evidence for this reaction comes from the work of Hanst and Calvert [88] who found that the yield of methanol formed in the pyrolysis at 200°C of dimethyl peroxide was greatly reduced by the addition of oxygen.

Kinetic tracer studies have been applied to the problem of the determination of the initial source of methanol. Neiman, Efremov and Serdyuk [89] have added $^{14}CH_3CHO$ and $^{14}CH_3N = NCH_3$ to propylene/oxygen mixtures at 315°C and have found that 75% of the methanol arises from acetaldehyde, a primary product of the oxidation of propylene, and that 75% of the acetaldehyde gives methanol. The experiments with azomethane established that at least some of the methanol can come from methyl radicals which also give formaldehyde and methane. Although these results establish the molecular precursor of methanol as acetaldehyde, they do not necessarily establish the free radical precursor as methoxy. In oxidations where acetaldehyde is only a minor product as in isobutane and ethane oxidations, the results of Neiman et al. cannot explain the formation of methanol.

Several workers [90] have concluded that methanol may result from the oxidation of methyl radicals. Various mechanisms were proposed for the formation of methanol and all were similar in that they postulated the intermediate formation of methyl peroxy and methoxy radicals. Raley, Porter, Rust and Vaughan [90] concluded that between 120°C and 160°C the following scheme could explain the formation of methanol from methyl radical oxidation.

$$CH_3 + O_2 = CH_3O_2 \qquad (17)$$

$$2CH_3O_2 = 2CH_3O + O_2 \qquad (18)$$

$$CH_3O + CH_3O = CH_3OH + CH_2O \qquad (19)$$

Although this mechanism may operate at low temperatures when the radical concentrations are high, it is unlikely to take place at higher temperatures where the concentration of methyl peroxy radicals is low and, as a result of their low concentration, methyl peroxy radicals will decompose to formaldehyde and OH in preference to disproportionation.

Wells [91] found that at 320°C methanol could be formed by the oxidation of methyl radicals. Addition of acetaldehyde to ethane/oxygen mixtures increased the yield of methanol and the yield of methanol from the oxidation of acetaldehyde alone was increased by the presence of ethane in the system. These observations were included in the scheme,

$$CH_3 + O_2 = CH_2O + OH \qquad (9) \quad \Delta H = -70 \text{ k cal.}$$

$$OH + CH_3CH_3 = CH_3OH + CH_3 \qquad (20) \quad \Delta H = -6 \text{ k cal.}$$

$$\text{cf. } OH + CH_3CH_3 = C_2H_5 + H_2O \qquad (21) \quad \Delta H = -37 \text{ k cal.}$$

This scheme accounts for the methanol formed in the initial stages of ethane oxidation when none of the products formed could give rise to methoxy radicals. However, hydroxy radicals are formed in the initial stages by the reaction

$$C_2H_5 + O_2 = C_2H_4O + OH \qquad (22)$$

and if OH radicals initiated the above chain the formation of methanol could be explained. A similar mechanism could operate in isobutane oxidation where OH radicals are formed by the decompocition of butyl peroxy radicals to isobutene oxide and OH. It must be pointed out that the above scheme implies that abstraction of CH_3 from ethane has a lower activation energy than abstraction of H. For this to be so, reaction (20) must have a lower activation energy than reaction (21) although the exothermicity of (21) is much greater than that of (20).

Once a good hydrogen donor is available in the system, e.g. formaldehyde or higher aldehydes which have C-H bonds about 10 k cal. weaker [92] than hydrocarbon C-H bonds, methanol is formed by the reaction

$$CH_3O + CH_2O = CH_3OH + CHO \qquad (23)$$

This reaction has been shown to occur at room temperature [84].

The formation of methane is determined by the result of a competition between H abstraction by, and oxidation of, methyl radicals. The possible reactions of methyl radicals in isobutane oxidation are

$$CH_3 + O_2 = CH_2O + OH \qquad (9) \quad \Delta H = -50 \text{ k cal.}$$

$$CH_3 + iC_4H_{10} = t\,C_4H_9 + CH_4 \qquad (10) \quad \Delta H = -12 \text{ k cal.}$$

As methane is formed in isobutane oxidation only when the concentration of oxygen is very low, reaction (10) cannot be important in isobutane oxidation at 300°C.

Carbon monoxide and carbon dioxide are both initial products of isobutane oxidation. In the later stages of the reaction, formation of CO greatly exceeds that of CO_2 and CO is then the major product of the oxidation. At this stage of the oxidation, formation of carbon oxides can be explained by extensive degradation of the hydrocarbon molecule. Tipper and Skirrow [93] have reviewed the existing data for the yield of carbon oxides in the oxidations of hydrocarbons and aldehydes and have shown that at constant temperature the ratio CO/CO_2 decreases as the fuel:oxygen ratio decreases. At constant mixture composition, this ratio increases with temperature. The latter relationship is clearly observed in this work on isobutane oxidation. These general observations are explained by a scheme involving the oxidation of the intermediate aldehyde. The strength of the aldehydic C-H bond is about 10 k cal. less than that of a primary C-H bond and aldehydes thus oxidise faster than the parent hydrocarbon. The formation of carbon oxides takes place according to the scheme outlined below

$$RCHO + O_2 = RCO + HO_2 \qquad (24)$$

$$RCO = R' + CO \qquad (25)$$

$$RCO + O_2 = RCO_3 \rightarrow CO_2 + \text{products} \qquad (26)$$

As the oxygen/fuel ratio increases the rate of reaction (26) relative to reaction (25) increases thus giving a decrease in the CO/CO_2 ratio. At higher temperatures, decomposition of RCO is preferred to oxidation and an increase in the CO/CO_2 ratio results. As R increases, the stability of RCO decreases and as the series of hydrocarbons is ascended higher yields of CO relative to CO_2 are found. Such a scheme cannot explain the formation of CO_2 in the oxidation of formaldehyde as reaction (26) is replaced by

$$HCO + O_2 = CO + HO_2 \qquad (15)$$

This replacement explains this high CO/CO_2 ratios which result from formaldehyde oxidation. In certain cases, the mechanism cannot be the only mode of formation of CO and CO_2.

While this mechanism may explain the formation of CO and CO_2 in the later stages of isobutane oxidation, it cannot explain the initial yields of CO and CO_2 which are much greater than the initial yields of any aldehyde with the exception of formaldehyde. Knox [50] has found that CO is also an initial product of the oxidation of propane and has discussed the mode of formation in detail. Since the formation of CO and CO_2 from secondary oxidation of aldehydes is at least second order in reaction products, the initial CO and CO_2, cannot be formed by this means. Knox has also shown that the initial formation of CO is not a result of secondary oxidation of propylene. The remainder of the observations made by Knox could equally well apply to the results of the present work on isobutane oxidation. As the yield of CO is independent of the hydrocarbon:oxygen ratio and is independent of the rate of reaction, it must be produced from a series of reactions none of which is more than first order in reaction products. Scrutiny of the results suggests that one alkyl peroxy radical results in the formation of one molecule of CO. There are two possibilities for the formation of CO. It may be formed from the surface oxidation of an alkyl peroxy radical or one of its decomposition products such as an aldehyde or by a series of gas phase reactions involving the progressive stripping of a free radical. The latter possibility is unlikely as some highly improbable reaction steps are necessary.

e.g. $CH_3O + O_2 = CHO + H_2O_2$ (27)

$CHO + O_2 = CO + HO_2$ (15)

Knox has shown that it is unlikely that surface oxidation of the branching agent is the source of CO as this necessitates shorter chain lengths than are indicated by the kinetic experiments he carried out on propane oxidation. This does not rule out the possibility that some other product diffuses to the walls and produces CO. Since the yields of all other aldehydes are low, it is likely that CH_2O is the source of the initial CO. If this reaction occurs in the gas phase, it is a branching reaction. The rate of the reaction is initially slow and it is likely that CO arises from surface oxidation of formaldehyde.

The large amount of CO_2 which was found in the isobutane oxidation in a silver plated reaction vessel suggests that at least part of the CO_2 formed in oxidation in Pyrex vessels may occur by heterogeneous processes. This would fall into line with results observed in the oxidation of cyclopentane [94] and methyl cyclopentane [95]. The CO/CO_2 ratio in the oxidation of cyclopentane was much greater in a boric acid coated vessel than in a Pyrex vessel. Much less CO_2 was found in the boric acid vessel. Pyrex was a more efficient catalyst for the decomposition.

$$\text{cyclopentyl peroxy} \longrightarrow nC_4H_9 + CO_2$$

This observation suggests that the initial yield of CO_2 in isobutane oxidation may result partly from wall decomposition of butyl peroxy radicals.

The high concentrations of acetone and carbon oxides in the later stages of isobutane oxidation have been shown to be partly due to the oxidation of primary products, isobutene and aldehydes. Evidence has been put forward to indicate that the formation of CO and CO_2 in the initial stages may take place as a result of wall processes involving the surface oxidation of formaldehyde and decomposition of butyl peroxy radicals respectively.

2. The nature of the radical attacking hydrocarbons.

In many studies of alkane oxidation, the yields of olefin have been initially roughly equal to the yields of $H_2O + H_2O_2$. The formation of an olefin and hydrogen peroxide has been accounted for by the HO_2 radical scheme given below.

e.g. for propane

$$C_3H_7 + O_2 = C_3H_6 + HO_2$$

$$C_3H_8 + HO_2 = C_3H_7 + H_2O_2$$

However, there are serious objections to such a scheme. Foner and Hudson [73] have redetermined the bond strengths D $[H\text{-}O_2]$ and D $[H - OOH]$ by the electron impact method. Their values of D $[H - O_2] = 45.7 \pm 2$ k cal. and D $[H - OOH] = 89 \pm 2$ k cal. are now generally accepted. As the strengths of C-H bonds in alkanes range from 90 to 98 k cal., the abstraction reactions of HO_2 with alkanes are all endothermic and may have activation energies a few k cal. higher than their endothermicities. Hence, the selectivity of HO_2 attack on alkanes should be similar to that of Br since the bond strength D $[H - Br]$ is 87 k cal.

Competitive oxidation studies [74, 96] have shown that between 320°C and 495°C the radical or radical mixture attacking ethane, propane, cyclopropane, isobutane, and neopentane has a selectivity greater than Cl but less than CF_3, CH_3O or CH_3. The authors showed that the relative rates of oxidation of propane and ethane in mixtures of the two hydrocarbons differed by a factor of 2.3. The relative rates of attack of Cl, CH_3O and Br on these hydrocarbons are 2.0, 3.0 and 10 at 350°C. Therefore, if only the results of those competitive experiments are considered, OH is the most likely attacking radical as it has a reactivity comparable to that of Cl [97].

The nature of the radical attacking hydrocarbons was studied by comparison of the rates of removal of isobutane and propane in a competitive oxidation at 300°C. Before discussing the experimental results, it is useful to derive the equations used for the evaluation of the relative rate constants a) by the product method and b) by the consumption method.

The expression for the relative rate constants for the removal of isobutane and propane by an attacking radical can be deduced by consideration of the scheme below. The hydrocarbon in each case is removed by a radical X which may be either OH or HO_2.

i.e. for isobutane

$$iC_4H_{10} + X = C_4H_9 + HX \qquad k_1$$

$$C_4H_9 + O_2 = C_4H_8 + HO_2 \qquad k_2$$

for propane

$$C_3H_8 + X = C_3H_7 + HX \qquad k_3$$

$$C_3H_7 + O_2 = C_3H_6 + HO_2 \qquad k_4$$

$$\frac{d}{dt}[C_4H_8] = k_2[C_4H_9][O_2] = k_1[iC_4H_{10}][X] = \frac{-d}{dt}[iC_4H_{10}]$$

and $$\frac{d}{dt}[C_3H_6] = k_4[C_3H_7][O_2] = k_3[C_3H_8][X] = \frac{-d}{dt}[C_3H_8]$$

$$\frac{\frac{d}{dt}[C_4H_8]}{\frac{d}{dt}[C_3H_6]} = \frac{\frac{-d}{dt}[iC_4H_{10}]}{\frac{-d}{dt}[C_3H_8]} = \frac{k_1[X][iC_4H_{10}]}{k_3[X][C_3H_8]}$$

$$\frac{k_1}{k_3} = \frac{\frac{d}{dt}[C_4H_8][C_3H_8]}{\frac{d}{dt}[C_3H_6][iC_4H_{10}]} = \frac{[C_4H_8][C_3H_8]}{[C_3H_6][iC_4H_{10}]} \qquad (A)$$

If the integrated form of the equation for hydrocarbon consumption is used, the resulting equation for the rate constant ratio is

$$\frac{k_1}{k_3} = \frac{\left[\log \left[iC_4H_{10}\ \text{initial}\right] - \log \left[iC_4H_{10}\ \text{final}\right]\right]}{\left[\log \left[C_3H_8\ \text{initial}\right] - \log \left[C_3H_8\ \text{final}\right]\right]} \quad (B)$$

Comparison of the two expressions shows that the rate constant ratios obtained by the two methods are representative of different extents of reaction. The product method can be used at very low alkane conversions since the accuracy depends on the direct measurement of the pressures of isobutene and propylene. Equation (B) shows that the consumption method depends on the subtraction of pressures of similar magnitudes and at low alkane conversions is inaccurate. Hence, at least 10% conversions of the alkanes are required for reasonable accuracy and normally the alkane consumptions are about 20% of the initial alkane pressure.

Results obtained from the oxidation of a 2:2:1 mixture of isobutane: propane:oxygen at 300°C are shown in Tables 35 and 36. In these tables, the accuracy of a few of the experimental rate constant ratios may be low. The propylene concentration term in the rate constant ratio expression (A) is the amount of propylene actually analysed less allowances for a) propylene present as an impurity in the propane and b) the yield of propylene from isobutane oxidation. The yield of propylene from isobutane oxidation in the competitive system was taken as the yield of propylene in a 2:1 isobutane:oxygen mixture at 225 mm at 300°C. Thus, at low propane conversion, propylene pressures of similar magnitudes had to be subtracted from each other and the rate constant ratios at low conversions of propane may be less accurate than those at higher conversions. However, when the percentage conversion of propane is greater than 0.4% (i.e. 0.3 mm of propylene has been formed), the error in the ratio is certainly less than 5% although at extremely low conversions, approximately 0.04%, errors as great as 20% may result. The values of the rate constant

ratios, other than those of Run 43 (Table 35) do not show a decline as the extent of reaction increases, and in general, all values lie between 2.1 and 3.

Since the rate constant ratio expression (A) deduced earlier is valid only if the individual alkyl radicals react with oxygen to produce equivalent fractional yields of olefins, the initial % yield of olefin in propane oxidation was required. The results of the oxidation of a 2:1 propane:oxygen mixture at 225 mm at 300°C showed (Figure 46) that 80% of the propane consumed is initially converted to propylene. This set of experiments was also used as a check on the competitive experiments. As the propane used in this oxidation contained about 1.6% isobutane as impurity, isobutene was detected. In this reaction, the yield of propylene from isobutane oxidation is negligible and no correction of the propylene pressure for propylene formed from isobutane is necessary. The initial concentrations of propane, isobutane and propylene are determined by analysis of the initial propane-oxygen mixture. Experimental values of the rate constant ratio lay in the range 2.6 to 3.5.

If HO_2 were the radical attacking the hydrocarbons, the relative rates of removal of hydrocarbons should be similar to those for the relative rates of removal by Br attack. The theoretical rate constant ratio for Br attack on isobutane and propane at 300°C has been calculated using literature values for the rates of attack of Br atoms on primary, secondary and tertiary C-H bonds.

Fettis, Knox and Trotman-Dickenson [98] give the following data for Br atom attack on the specified bonds.

Bond attacked	log A/H atom ($mole^{-1} cc^{3}$ sec^{-1})	log A/mole ($mole^{-1} cc^{3}$ sec^{-1})	A.E. k cal.
primary C-H in C_2H_6	13.1	13.9	13.4
neo C_5H_{12}	13.2	14.2	14.3
secondary C-H in C_3H_8	13.4	13.7	10.1
tertiary C-H in iC_4H_{10}	13.3	13.3	7.5

Thus, at 300°C, in a 1:1 mixture of C_3H_8 and iso C_4H_{10} the relative rate of removal of the hydrocarbons by Br atom attack is given by

$$\frac{\text{Rate of removal of isobutane}}{\text{Rate of removal of propane}} = \frac{9k_p + k_t}{6k_p + 2k_s} = \frac{k\,(\text{isobutane})}{k\,(\text{propane})} \qquad (C)$$

where k_p (iso) is the rate constant for Br attack on a primary C-H in isobutane,

k_p (prop) " " " " " " " " " " " " propane,

k_s " " " " " " " " " " secondary C-H in propane,

k_t " " " " " " " " " " tertiary C-H in isobutane,

and k (isobutane) and k (propane) are the overall rate constants for Br attack on isobutane and propane respectively.

The rate constants are given numerically by

$$k_p\,(\text{iso}) = 10^{13.2} \exp \frac{-14{,}300}{RT}, \qquad k_p\,(\text{prop}) = 10^{13.1} \exp \frac{-13{,}400}{RT}$$

$$k_t = 10^{13.3} \exp \frac{-7{,}500}{RT}, \qquad k_{sec} = 10^{13.4} \exp \frac{-10{,}100}{RT}$$

A primary C-H bond in isobutane has been taken as equivalent to a primary C-H bond in neopentane while a primary C-H bond in ethane has been taken as equivalent to a primary C-H in propane.

Substitution in (C) gives $\frac{k\ (\text{isobutane})}{k\ (\text{propane})}$ = 3.70 at 300°C

Similar calculations have been made on data of Anson, Fredricks and Tedder [99] for the competitive bromination of iso- and n- butane. They have shown that at 400°K the reactivities of primary, secondary and tertiary atoms to Br attack are in the ratio 1:82:1600. Calculation of the relative reactivities of these types of atoms at 300°C and application of (C) gives, assuming that the A factors for Br attack on various types of atoms are equal,

$$\frac{k\ (\text{isobutane})}{k\ (\text{propane})} = 3.68$$

This value is in good agreement with that obtained from the data of Fettis, Knox and Trotman-Dickenson. Since the bond strength D [H-Br] is less than that of D [H-OOH], the rate constant ratio for HO_2 attack would be slightly lower than that for Br attack as HO_2 is probably less selective than Br. If OH were the radical attacking the hydrocarbons, the rate constant ratio would be about 1:1. Therefore, on the basis of the experimental rate constant ratios given in Tables 35 and 36, it is concluded that HO_2 radical attack is responsible for the removal of the alkanes in the initial stages of slow oxidation. If an increase in OH concentration occurred during the course of the reaction, the rate constant ratio would decrease from 3 to 1 as the extent of reaction increased. The results of the present work yield a rate constant ratio which is approximately

25-3 and, although the experimental results are not sufficiently precise to exclude any decrease in rate constant ratio, little indication has been found of a decrease in rate constant ratio as the extent of reaction increases.

Falconer, Knox and Trotman-Dickenson [74] determined the rate constant ratio for a particular set of experimental conditions by the consumption method. In their experiments, about 20% of each alkane was removed. At this extent of reaction, secondary oxidation is certainly taking place and the radical or radicals attacking the alkanes in the later stages may not be those which attack the alkanes in the earlier stages. Further evidence for this comes from the dependence of the rate constant ratio at a fixed temperature on the oxygen: hydrocarbon ratio. As the oxygen: hydrocarbon ratio increases, the rate constant ratio increases*, i.e. the relative rate of consumption of the hydrocarbons increases towards unity and the radical or radicals removing the hydrocarbon become less selective. The overall relative rate constant ratio for the removal of two hydrocarbons therefore depends on the extent of reaction. At high temperatures, the dependence of k_1/k_3 on oxygen:hydrocarbon ratio was much greater that at low temperature, again indicating that, as product distribution varies with temperature, product reaction leads to radicals which attack the hydrocarbons. However, Falconer, Knox and Trotman-Dickenson have

* The rate constant ratios of Falconer, Knox and Trotman-Dickenson are the reciprocals of those obtained in the present work. In our work as HO_2 attack changes to OH attack, k (isobutane)/k (Propane) goes from 3 to 1 but k (propane)/ k (isobutane) as used by Falconer et al. goes from 0.3 to 1.

studied the effects of additives on the rate constant ratio for propane:ethane mixtures and have found little variation in the rate constant ratio. This result suggests that the radical attacking the hydrocarbons in the later stages of the reaction are not formed as a result of oxidation of primary products such as ethylene, propylene, methanol and acetaldehyde. Falconer et al. have found the rate constant at zero $[O_2]/[RH]$ by extrapolation and have suggested that this ratio refers to the radical attacking the hydrocarbon in the initial stages. Since all their experiments refer to about 20% conversion of the alkanes and no low $[O_2]/[RH]$ mixtures have been studied, it is likely that their rate constant ratio refers to about 10% reaction.

The initial stage product method of competitive oxidation gives a less ambiguous picture of the nature of the radical attacking the alkanes in the initial stages. HO_2 attack is then operative. In the later stages of the reaction, the selectivity of the attacking radical or radicals clearly decreases and an increase in the concentration of OH relative to HO_2 could explain this.

Knox and Wells [51] have proposed that OH radicals may be formed from disproportionation of HO_2 radicals and have discussed the consequences of this possible reaction on the oxidation of ethane. Heterogeneous decomposition of hydrogen peroxide is usually put forward as the reason for the yields of hydrogen peroxide being considerably less than those of the olefin in the initial stages. Hydrogen peroxide may be formed from two reactions

$$HO_2 + RH = H_2O_2 + R \qquad (5)$$

and

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad (6)$$

Reaction (6) is important in the oxidation of hydrogen in boric acid coated vessels at 500°C [45]. At this temperature, the hydrogen peroxide quickly dissociates and the reaction proceeds by means of a "degenerate chain" in which free radical and molecular intermediates alternate as reactive species. Sampson [100] has shown that a similar mechanism applies in the oxidation of ethane at 600°C. The degenerate chains for both reactions can be written.

$$OH + C_2H_6\ (H_2) = H_2O + C_2H_5\ (H) \qquad (7)$$

$$C_2H_5\ (H+M) + O_2 = C_2H_4\ (M) + HO_2 \qquad (8)$$

$$2HO_2 = H_2O_2 + O_2 \qquad (6)$$

$$H_2O_2 + M' = 2OH \qquad (9)$$

(the reactants and products in brackets apply to the hydrogen-oxygen reaction). The overall rates of both reactions are close to the independently measurable rate of homogeneous pyrolysis of the hydrogen peroxide present. If such a scheme operated in the low temperature oxidation, the low yields of hydrogen peroxide could be explained by the attack of OH as well as HO_2 on the hydrocarbon. Such attack would result in the formation of water and hydrogen peroxide whereas attack by HO_2 alone would result in only hydrogen peroxide formation. At 300°C, however, the rate of pyrolysis of the peroxide is much too low [101] so that reaction (6) cannot be the main remover of HO_2 if the overall reactions are chain reactions.

The results of the work on the hydrogen-oxygen system and methane oxidation have suggested that the activation energies of the reactions of HO_2 with H_2 and CH_4 are close to those of Br atoms with H_2 and CH_4. The dependence of the rate of slow oxidation of hydrogen on the hydrogen mole fraction at 500°C requires the introduction of a "regeneration reaction"

$$HO_2 + H_2 = H_2O_2 + H \qquad (10)$$

Although the HO_2 concentration must be much higher than the OH concentration, this reaction never accounts for more than 5% of the hydrogen consumption. From the overall rate of reaction and assuming reactions (6) and (10) have steric factors of unity, E_{10} is calculated to be about 27 k cal. If the steric factor of (10) were 10^{-3}, E_{10} = 17 k cal.

In the oxidation of methane [102], the formaldehyde concentration passed through a maximum during the reaction. This maximum increased with temperature with an activation energy of about 8 k cal. According to their mechanism, this energy is given by

$$E_F = \tfrac{1}{2}\left[E(HO_2 + CH_4) + E(OH + CH_4) - E(HO_2 + CH_2O) - E(OH + CH_2O)\right]$$

Since the activation energies of the two OH radical reactions are probably low, the difference in the activation energies of the HO_2 radical reactions must be close to 16 k cal. The steps in the mechanism involving HO_2 attack on CH_4 and CH_2O are

$$HO_2 + CH_4 = H_2O_2 + CH_3 \qquad (11) \qquad \Delta H = +13 \text{ k cal.}$$

$$HO_2 + CH_2O = H_2O_2 + CHO \qquad (12) \qquad \Delta H = -4 \text{ k cal.}$$

It is likely that the activation energy of (11) is a few k cal. greater than 13 k cal. while reaction (12) probably has a low, near zero activation energy. Thus, $E(HO_2 + CH_4) \geq 16$ k cal. These values of 17 k cal. for $E(HO_2 + H_2)$ and 16 k cal. for $E(HO_2 + CH_4)$ compare with 20 and 18 k cal. for the corresponding reactions of Br atoms. It is thus likely that $E(HO_2 + iC_4H_{10}) \approx 7$ k cal.

Since the formation of HO_2 along with the olefin in reaction (8) seems unavoidable, Knox and Wells [51] proposed that a key reaction in hydrocarbon oxidation may be the conversion of HO_2 to OH by the reaction

$$2HO_2 \longrightarrow [HOO - OOH] \longrightarrow 2OH + O_2 \qquad (13)$$

This reaction is analogous to those of alkyl peroxy radicals to give alkoxy radicals and oxygen [84, 85] but, whereas the latter are almost certainly endothermic since they occur at room temperature, reaction (13) is 10 k cal. endothermic. The difficulty of the endothermicity can be overcome if it is supposed that hydrogen tetroxide is a true intermediate which decomposes preferentially to OH and O_2 rather than to HO_2. Laidler and Steel [103] have shown that decomposition into three fragments might be expected to have an A factor higher by between 10^2 and 10^3 than that of a normal unimolecular decomposition. This unusually high A factor could counteract the adverse activation energy.

Knox and Wells also suggested that the recombination reaction of HO_2 could explain the effects of inert gas addition to alkane oxidations. Generally inert gas affects the length of the induction period but has little effect on the main part of the reaction. Reaction (6) for the conversion of HO_2 to OH is second order in HO_2 and will only occur when the HO_2 concentration is high. In the absence of mutual reaction of HO_2 by (6) or (13) the radicals will tend to diffuse to the walls of the reaction vessel attacking a small number of alkane molecules on the way. Thus, a diffusion controlled chain might be expected in the initial stages. In the later stages of the oxidation when the rate of reaction has risen sufficiently this diffusion controlled chain becomes a gas phase terminated chain and the addition of inert gas has no effect on the rate of reaction.

The time of diffusion to the walls of HO_2 in the reaction vessel used in this work on isobutane is about 2 seconds and the rate constant of reaction (14)

$$HO_2 + iC_4H_{10} = tC_4H_9 + H_2O_2 \qquad (14)$$

is probably given approximately by

$$k_{14} = 10^9 e^{-7,500/RT} = 10^{6.1} \text{ mole}^{-1} \text{ l sec}^{-1} \text{ at } 573\ ^\circ K$$

$$\text{Chain length} = \frac{\text{Rate of propagation}}{\text{Rate of termination}} = \frac{k_{14}[HO_2][iC_4H_{10}]}{k_t[HO_2]} = \frac{k_{14}[iC_4H_{10}]}{k_t}$$

Since $k_t = 0.5 \text{ sec}^{-1}$, the chain length at 300°C with an isobutane concentration of 150 mm (4.2×10^{-3} mole l^{-1}) is 11,300.

Knox and Wells deduced a chain length of 90 during the induction period of ethane oxidation at 362°C. As the time of diffusion of HO_2 to the walls is approximately the same as in the present work, the increase in the length of the chain during the induction period of isobutane oxidation can be attributed to the fact that the rate of attack of HO_2 on isobutane is about 100 times greater than the rate of HO_2 attack on ethane.

As the reaction accelerates, the HO_2 concentration rises and eventually mutual reaction may occur. The chain length will then decrease due to reaction (6).

The importance of HO_2 attack on isobutane may be assessed as follows. It is assumed that HO_2 is involved only in reactions (6) and (14). Baldwin considers that $k_6 = 10^{10}$ mole $^{-1}$ l sec $^{-1}$ which is slightly less than the collision number. The maximum rate of removal of isobutane in the 2:1 isobutane:oxygen mixture at 362°C is 1 mm/min = 0.017 mm/sec.

Denoting reaction rates by R_{14}, R_6

$$R_{14} = 0.017 \text{ mm/sec} = k_{14} [HO_2] [RH]$$

$$R_6 = k_6 [HO_2]^2$$

$$R_6/R_{14} = k_6 R_{14}/(k_{14} [RH])^2 = 2.1 \times 10^{-4}$$

taking $k_{14} = 10^{6.1}$, $k_6 = 10^{10}$ and $[RH] = 3.7 \times 10^{-3}$ units being mole l^{-1} sec. Thus, even at the maximum HO_2 concentration, recombination of HO_2 cannot compete with HO_2 abstraction from isobutane and thus HO_2 chains can account for the observed rate of removal of isobutane if termination could only occur by reaction (6). If the mutual reaction of HO_2 radicals proceeds by reaction (13) then for every HO_2 which terminates the reaction by (13) there will be a number of OH radicals which will attack isobutane. On the basis of the initial yields of H_2O_2 and H_2O, k_{13}/k_6 is unlikely to be greater than 10. As the chains are unlikely to be short, it is possible that the slow rate of acceleration of the oxidation is due to the small proportion of chain steps which form branching agent rather than to the shortness of the chains.

This result contrasts with the conclusion reached by Knox and Wells [51]. They found that gas phase termination by HO_2 recombination could compete with HO_2 attack on ethane at 362°C. Although such a recombination reaction is mathematically possible in ethane oxidation, the endothermicity of the reaction $HO_2 + HO_2 = 2OH + O_2$ and the fact that this reaction does not occur in isobutane oxidation make it unlikely that the recombination reactions of HO_2 are important in alkane oxidation.

As there is no doubt that the selectivity of the radical mixture attacking the hydrocarbon mixture in the later stages of oxidations is less than that attacking the hydrocarbons in the initial stages, the concentrations of less

selective radicals such as OH and CH_3O must increase as the oxidation proceeds. When the concentration of olefin is high, HO_2 may preferentially attack the olefin to give a radical which decomposes to a ring oxide and OH.

e.g. for isobutene.

$$(CH_3)_2\,C = CH_2 + HO_2 \rightarrow (CH_3)_2\,C(OOH)-CH_2 \rightarrow (CH_3)_2 - C(O)-CH_2 + OH$$

OH, being much less selective than HO_2, will preferentially attack the alkane on account of its higher concentration and give the reduction in selectivity observed in the competitive experiments of Falconer, Knox and Trotman-Dickenson. This suggestion may be checked by carrying out competitive alkane oxidations in the presence of added olefin. Oxidation of 2:2:1 mixtures of isobutane: ethane:oxygen at 300°C at 200 mm with 5 mm of added propylene would result in a rate constant ratio much lower than calculated for HO_2 attack if conversion of HO_2 to OH occurred through the olefin. Added propylene would not interfere with the determination of the ratio k (isobutane)/ k (ethane) by the product method.

Competitive propane-isobutane oxidations at 300°C have shown that the HO_2 radical chain is responsible for hydrocarbon removal in the initial stages of alkane oxidations. Disproportionation of HO_2 to form OH has been shown to be unimportant in isobutane oxidation and it is unlikely that this reaction can be responsible for the reduction in selectivity of the hydrocarbon attacking radicals in the later stages of alkane oxidations.

3. The initial stages of the oxidation of Propane.

The oxidation of propane was carried out principally to determine the fraction of propane which was initially converted to propylene. 78% of the propane consumed was converted to propylene in the initial stages. Small amounts of (in decreasing order of magnitude) acetaldehyde, propylene oxide, acetone, methanol, ethylene, ethanol and propionaldehyde were also found. The identities of the oxygenated compounds are in good agreement with the results of less detailed studies by earlier workers [104] who generally detected only acetaldehyde, ethylene and methanol. The high conversion of propane to propylene is in agreement with the results of Knox [87] and the formation of propylene occurs by an HO_2 radical chain.

i.e. $C_3H_8 + HO_2 = C_3H_7 + H_2O_2$ (1)

$C_3H_7 + O_2 = C_3H_6 + HO_2$ (2)

As HO_2 may abstract H from either a primary or secondary C-H bond, n-propyl and iso-propyl radicals are formed in the propagation steps. The radicals may also add oxygen to give propyl peroxy radicals which may isomerise and decompose to form the minor oxygenated products. Possible products from sec-propyl peroxy radicals are

a) $CH_3\underset{\underset{OO}{|}}{C}HCH_3 \longrightarrow CH_3\underset{\underset{OOCH_3}{|}}{C}H \longrightarrow CH_3CHO + OCH_3 \xrightarrow{C_3H_8} CH_3OH$

b) $CH_3\underset{\underset{OO}{|}}{C}HCH_3 \longrightarrow CH_3\underset{\underset{OOH}{|}}{C}HCH_2 \longrightarrow CH_3CH\!-\!CH_2 + OH$

c) $CH_3\,\underset{\underset{OO}{|}}{CH}\,CH_3 \longrightarrow CH_3\,\underset{\underset{OOH}{|}}{C}\,CH_3 \longrightarrow CH_3COCH_3 + OH$

Possible products from n propyl peroxy radicals are

d) $CH_3CH_2CH_2OO \longrightarrow CH_3CH_2CHOOH \longrightarrow CH_3CH_2CHO + OH$

C_3H_8

e) $CH_3CH_2CH_2OO \longrightarrow CH_2OOC_2H_5 \longrightarrow CH_2O + C_2H_5O \longrightarrow C_2H_5OH$

f) $CH_3CH_2CH_2OO \longrightarrow CH_2CH_2OOCH_3 \longrightarrow C_2H_4 + CH_3OO$

The relative amounts of products can be explained in some cases. As HO_2 is more likely to attack a secondary H atom than a primary H atom, the concentration of sec-propyl radicals will be about ten times that of n-propyl radicals. A similar difference can be expected between the concentrations of n-propyl and isopropyl peroxy radicals. Hence, the yields of acetaldehyde, propylene oxide, methanol and acetone would be expected to be greater than those of propionaldehyde, ethanol and ethylene. This is shown to occur by comparing the initial percentages of each product which are shown in Figure 46. Methanol and ethanol are formed in the reaction scheme by the abstraction of H from propane by methoxy and ethoxy respectively. The yield of methanol should be equal to that of acetaldehyde if every methoxy abstracted H. That the yield of methanol is lower than that of acetaldehyde is not unexpected since alkoxy radicals oxidise more easily than they abstract H. The source of initial methanol has been discussed in detail in the discussion of the slow oxidation of isobutane. Thus, the formation of oxygenated products in the low temperature oxidation of propane can be explained by the isomerisation reactions of propyl peroxy radicals although the yields of methanol and ethanol are only expected to be high in the later stages of the oxidation of oxygen weak mixtures.

4. Homogeneous and heterogeneous processes in isobutane oxidation.

The results obtained from isobutane oxidation at 270-330°C are so complex (Figures 52 and 53) that they cannot be explained by a simple mechanism as proposed by Zeelenberg. If product formation resulted from intramolecular decomposition of butyl peroxy radicals, the lines in Figure 52 would be parallel to the oxygen pressure axis and those in Figure 53 would show a slow unidirectional trend with increase in temperature. As the results of the present work could not be fitted to an Arrhenius equation and as the unusual results of Runs 55-58 (Figures 43-45) could not be explained other than by a change in the nature of the reaction vessel surface, further oxidations were carried out on widely varying reaction vessel surfaces and the changes in product distribution observed.

On acidic surfaces, boric acid and silicic acid, the yields of aldehydes are high and generally the fraction of minor products is increased on acidic surfaces. The ratio of major to minor products is little changed in going from clean Pyrex to a potassium chloride coated vessel but the yield of propionaldehyde is markedly reduced. Striking changes in the distributions of minor products with alteration in surface suggest that minor product formation is predominantly the result of heterogeneous processes.

Significant discrepancies between the results of different groups of workers on a particular hydrocarbon oxidation system support the suggestion that oxidations are not completely homogeneous. Zeelenberg [52], for a 2:1 isobutane:oxygen mixture at 300°C, has found that the initial product distribution is isobutene 80%, isobutene oxide 8%, propionaldehyde 4%, acetone 2.5% and propylene 4%. The results of the present work give a product distribution of isobutene 80%, isobutene oxide 4.5%, propionaldehyde 4.4%, acetone 2.7%, propylene 3.4%, acetaldehyde 2.6%, methacrolein 0.7% and isobutyraldehyde 1.8%.

Similar discrepancies occur in the results of Skirrow and Williams [105] and Hay and Knox [79] on isobutene oxidation at 300°C. Skirrow and Williams found that acetone and an equimolar yield of formaldehyde accounted for 70% of the olefin consumed. Hay and Knox found that the yield of formaldehyde is consistently less than that of acetone and that the difference in the early stages is equal to the yield of carbon monoxide. Skirrow and Williams also found that isobutyraldehyde was the next most important product and its isomer isobutene oxide was formed in only trace amounts. Isobutene oxide accounts, in a clean Pyrex reaction vessel, for about 17% of the organic product detected by Hay and Knox while the yield of isobutyraldehyde was very small below 300°C.

The high aldehyde yields obtained in oxidation on acidic surfaces agree with the results of Satterfield and Reid [72]. On acidic surfaces, the oxidation mechanism is complicated by the extremely fast isomerisation of isobutene oxide to isobutyraldehyde. At 300°C, 95% of the isobutene oxide present in a boric acid coated vessel is converted to isobutyraldehyde within one minute. Rapid isomerisation can probably account for the low initial yields of isobutene oxide on boric acid coated vessels. Such isomerisations also raise the question of alternative products. If isomerisation were very fast, isobutyraldehyde may be formed only from isobutene oxide. This is unlikely since, in a clean Pyrex vessel where the rate of isomerisation is at least 100 times slower than in a boric acid coated vessel, the initial yield of isobutyraldehyde is four times that of isobutene oxide.

The question of whether the whole oxidation process is heterogeneous now arises. Free radical chains are necessary to explain the formation of cool flames, autocatalysis, explosion limits, negative temperature coefficients and the actions of inhibitors and initiators in hydrocarbon oxidations. In

isobutane oxidation, minor product formation parallels major product (isobutene) formation and, hence, the heterogeneous processes involved must be closely associated with the homogeneous processes. Any heterogeneous processes must, therefore, involve free radicals formed in the gas phase. The mechanism proposed for the formation of major and minor products is as follows:

$$C_4H_9 + O_2 = C_4H_8 + HO_2 \quad (1)$$

$$iC_4H_{10} + HO_2 = C_4H_9 + H_2O_2 \quad (2)$$

$$C_4H_9 + O_2 = C_4H_9OO \quad (3)$$

$$C_4H_9OO \xrightarrow{\text{wall}} \text{complex mixture of oxygenated products} \quad (4)$$

The strong influence of the surface on the relative yields of minor products implies that they are formed predominantly in heterogeneous processes as the primary products are stable and the results cannot be explained as due to isomerisation of primary products. A fraction of the butylperoxy radical may in addition homogeneously give minor products and a proportion of isobutene.

For this mechanism to operate, it is necessary that the time of diffusion of a butyl peroxy to the walls must be less than the lifetime of the radicals with respect to its homogeneous first order decomposition or its bimolecular reaction with H donors.

The mean diffusion time for a molecule to travel a distance Δx is given by the Einstein equation

$$t = (\Delta x)^2 / 2D$$

The diffusion coefficient of a small peroxy radical in an oxidising mixture at 600°K and 200 mm pressure has been estimated from Maxwell's Equation to be about 1 cm^2 sec^{-1} [106, 107]. As the mean distance for diffusion to the

walls in a 500 ml spherical vessel is 2 cm, the mean diffusion time is about 2 sec.

The bond strength D(R-OO) in butyl peroxy radicals has been argued to be about 25 k cal. For decomposition of the peroxy radical into significant products, internal isomerisation is necessary either before or during the dissociation. Reactions in which isomerisation takes place in addition to simple bond breaking and bond forming require an activation energy greater by 10 k cal. than that required for simple bond breaking and bond forming [108]. Thus, the decomposition of a butylperoxy radical to minor products probably requires an activation energy of 35 k cal. The rate constant for a unimolecular decomposition is given by

$$k = 10^{13} e^{-E/RT} \qquad (5)$$

Substituting in (5) and writing $t = 1/k$ shows that the lifetime of the radical with respect to decomposition is of the order of 1 sec. This is likely to be a minimum value as no allowance has been made for an A factor lower than 10^{13}.

Rate constants for the gas phase abstraction reactions of peroxy radicals are not known. A large amount of data exists on these reactions in the liquid phase [22, 109], and, in general, gas phase rate constants do not differ greatly from those for the same reaction in the liquid phase if solvation is unimportant. The lifetime of the peroxy radical in the gas phase can probably be approximated reasonably accurately using liquid phase data. Liquid phase abstraction reactions by peroxy radicals have low steric factors of about 10^{-6} and activation energies with unsubstituted olefins and alkanes [109] of about 10 k cal. mole $^{-1}$. Applying these parameters to the gas phase, the rate constant for H abstraction is

$$k \approx 10^{5} e^{-10,000/RT} \text{ mole}^{-1} \text{ litre sec}^{-1}$$

The lifetime of this radical at a pressure of 200 mm alkane at 600°K is then

$$t = 1/kc \approx 10^{-5} \exp^{10,000/RT} \times 200 \text{ sec} \quad 10 \text{ sec.}$$

Thus, the lifetime of the peroxy radical with respect to H abstraction is comparable to the time of diffusion to the walls.

The lifetimes of the peroxy radical with respect to unimolecular decomposition and H abstraction reactions are not considerably less than the time of diffusion of a peroxy radical to the walls. Thus, the view that the heterogeneous processes involving peroxy radicals are important in hydrocarbon oxidation does not conflict with reasonable estimates of the rates of competing homogeneous processes.

According to the mechanism outlined earlier in this section, the ratio of major to minor products should be influenced by the addition of inert gas. At high pressures of inert gas, the diffusion time is greatly increased and the ratio of major products to minor products should increase. In the present study, only a small pressure of nitrogen was added to a 2:1 mixture of isobutane:oxygen and the product distribution compared to that of the initial mixture (Figures 33-36). An increase in the fractional yield of isobutene was noted -from 80% without N_2 to 85% in the presence of 75 mm N_2 - but this increase is small and, since the error in the calculation of the initial isobutene yield is about 2%, it is little greater than experimental error. Experiments at high pressures of inert gas (600 mm) would be invaluable in determining the proportion of the minor products which is formed in wall processes.

More useful information about surface processes could be obtained by carrying out a series of oxidations in reaction vessels of approximately constant volume but of varying surface/volume ratio. As the surface/volume ratio increases the proportion of the minor products should increase.

Isobutane oxidation at 300°C on a silver surface seems to be a particularly unusual reaction. Autocatalysis is eliminated and no aldehydes, which may be responsible for branching in the uncatalysed oxidations, are formed. The yield of isobutene, the expected product of homogeneous gas phase oxidation, was low compared to that of carbon dioxide indicating that the bulk of the reaction took place at the walls of the reaction vessel. The only oxygenated compounds formed were ring oxides which may result from a reaction analogous to that forming ethylene oxide from ethylene [110, 111]. Traces of isomeric butenes are probably due to the catalysed isomerisation of the isobutene initially formed. The nature of the wall process is uncertain but may be a molecular process between isobutane and oxygen or a free radical decomposition on the walls. Butyl radicals must certainly be produced to form isobutene but their fate on reaction with oxygen either in the gas phase or at the walls is unknown. One significant feature is that carbon dioxide can result from a heterogeneous process while the carbon monoxide yield in the same process is low. This feature indicates that CO is not formed by a surface process involving only isobutane and oxygen.

Oxidation of methanol [112] on a silver surface has been shown to be a completely heterogeneous process. Formaldehyde was formed which was desorbed into the gas phase. The homogeneous oxidation of formaldehyde as well as that of methanol was completely suppressed by the destruction of the active centres at the silver surface.

Since isobutane oxidation on a silver surface may well be due to a process independent of those occurring in the slow oxidation on a clean Pyrex vessel, no conclusion about the mechanism of the normal slow oxidation, apart from the possibility of heterogeneous formation of CO_2, may be drawn from the catalysed oxidation.

Isobutane oxidations in coated vessels have indicated that the formation of the minor products may result from heterogeneous processes. The lifetimes of the peroxy radical with respect to unimolecular and H abstraction reactions have been shown to be at least as great as the time of radical diffusion to the walls. Thus, in view of the experimental evidence, there seems little doubt that minor product formation results predominantly from heterogeneous processes.

5. Conclusion

Competitive propane/isobutane oxidations have shown that removal of the alkane in the initial stages occurs by an HO_2 radical chain. The view has been expressed that the low selectivity of the attacking radicals in the later stages of alkane oxidation does not result from recombination and disproportionation of HO_2 radicals to form OH and O_2.

The oxidation of isobutane in the temperature range, 270-330°C, has been shown to occur in the initial stages by an HO_2 radical chain, 80% of the isobutane consumed being converted to isobutene. Isobutene is formed by direct abstraction by O_2 from butyl radicals and minor products (acetone, propylene, propionaldehyde, isobutene oxide etc.) are formed from isomerisation reactions of butyl peroxy radicals. The temperature and fuel/oxygen dependences of the isobutene/minor product ratios can not be fully explained by a simple homogeneous mechanism. The wide variations in the initial yields of minor products with change in mixture composition and temperature has indicated that the minor products are not formed by a simple homogeneous scheme based on isomerisation and decomposition of butyl peroxy radicals.

Isobutane oxidations carried out in coated reaction vessels have shown that the minor products are formed predominantly in heterogeneous processes and a scheme has been proposed to account for this.

$$iC_4H_{10} + HO_2 = C_4H_9 + H_2O_2$$

$$C_4H_9 + O_2 = C_4H_8 + HO_2$$

$$C_4H_9 + O_2 = C_4H_9OO$$

$$C_4H_9OO \xrightarrow{\text{wall}} \text{complex mixture of minor products.}$$

The reaction vessel surface has been shown to play a much more important role in hydrocarbon oxidation than had previously been assumed. It is unwise to make any deduction from initial rate data as to the relative rates of supposedly homogeneous processes until considerably more work has been carried out on the role of surface in low temperature combustion.

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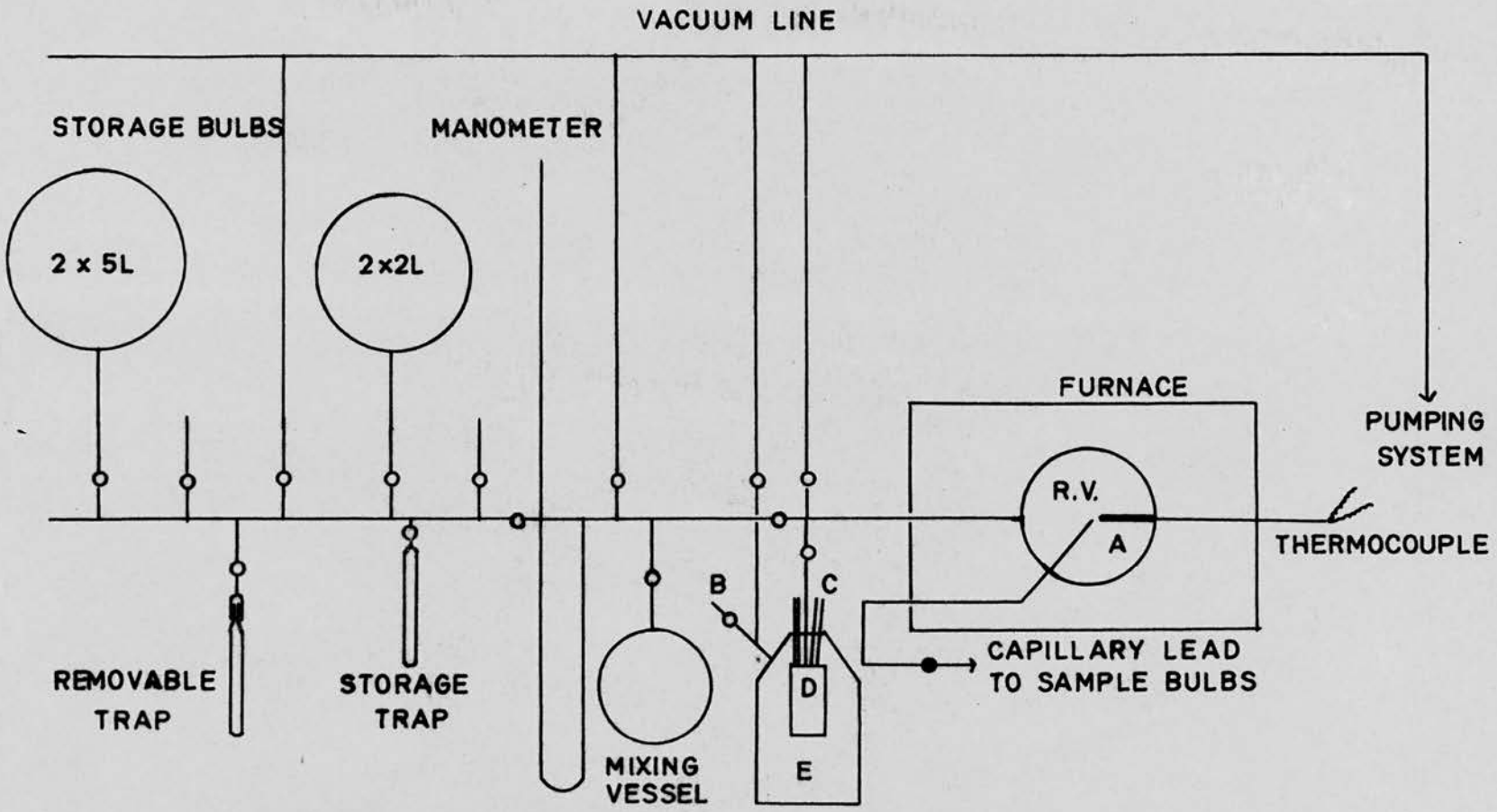
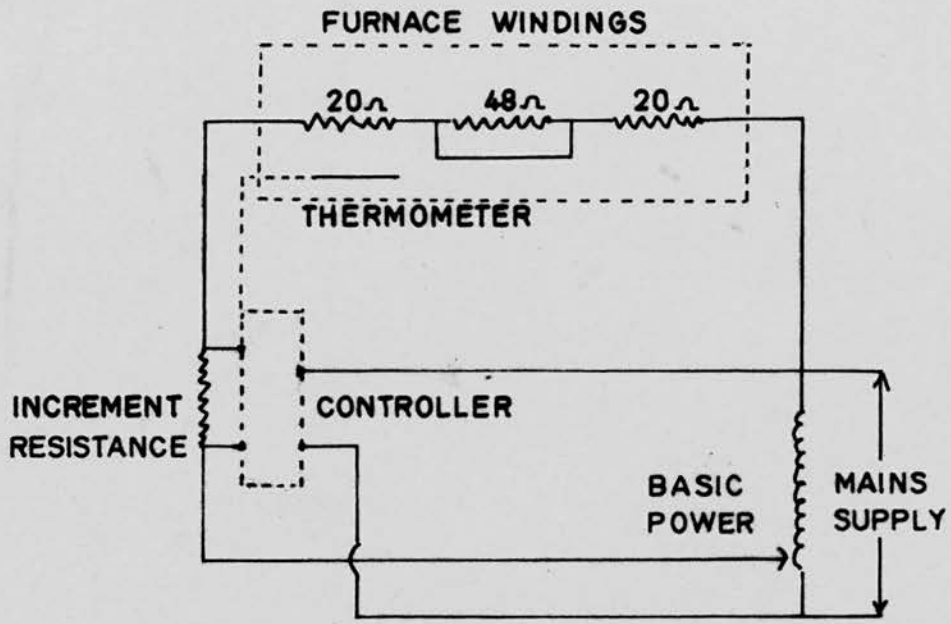


R.V. REACTION VESSEL
o HIGH VAC. TAP
● HONE VALVE
A THERMOCOUPLE POCKET
B AIR LEAK
C ELECTRICAL CONNECTIONS TO TRANSDUCER
D PRESSURE TRANSDUCER
E BACKING PRESSURE VESSEL

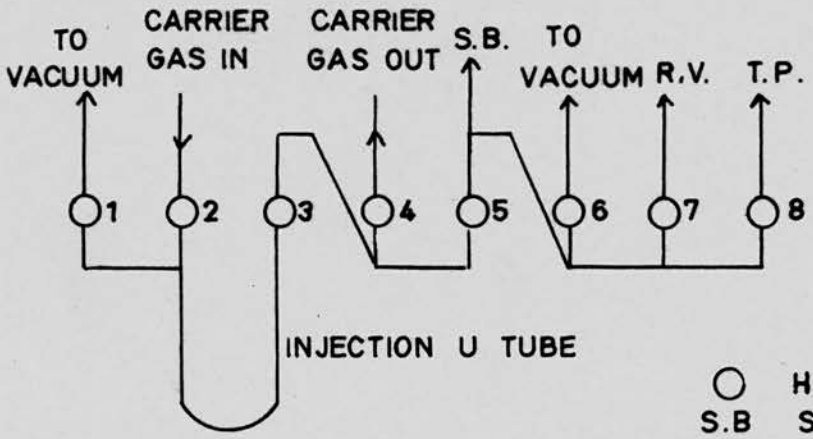
FIG.1 KINETIC APPARATUS

FIGURE 2



FURNACE CIRCUIT

FIGURE 3

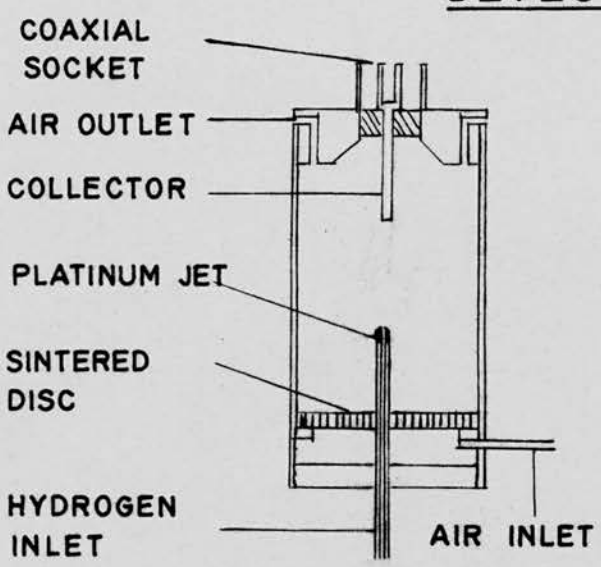


○ HONE VALVE
S.B SAMPLE BULBS
R.V. REACTION VESSEL
T.P. TOEPLER PUMP
3 ANTI-DIFFUSION TAP

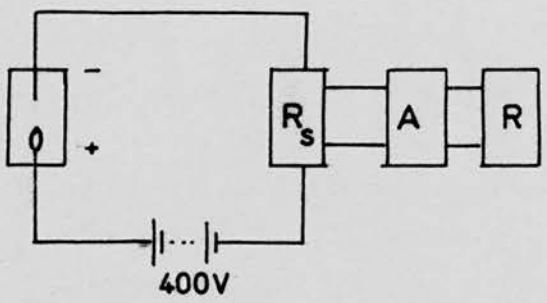
SAMPLING AND ANALYSIS MANIFOLD

FIG. 4.

DETECTORS

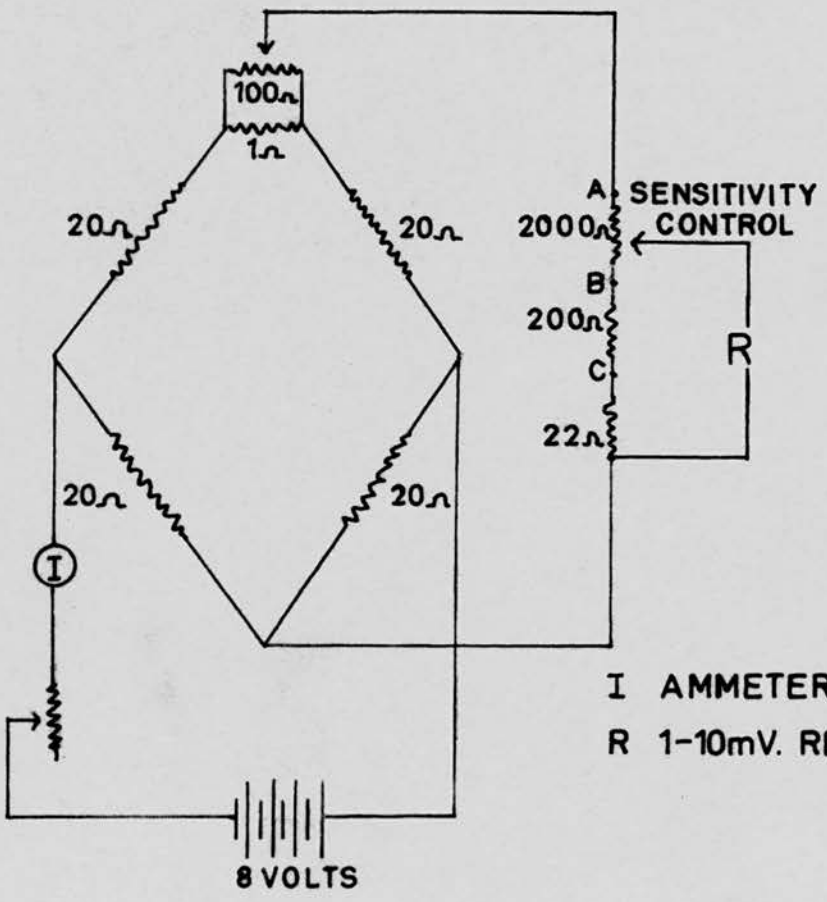


FLAME IONISATION DETECTOR



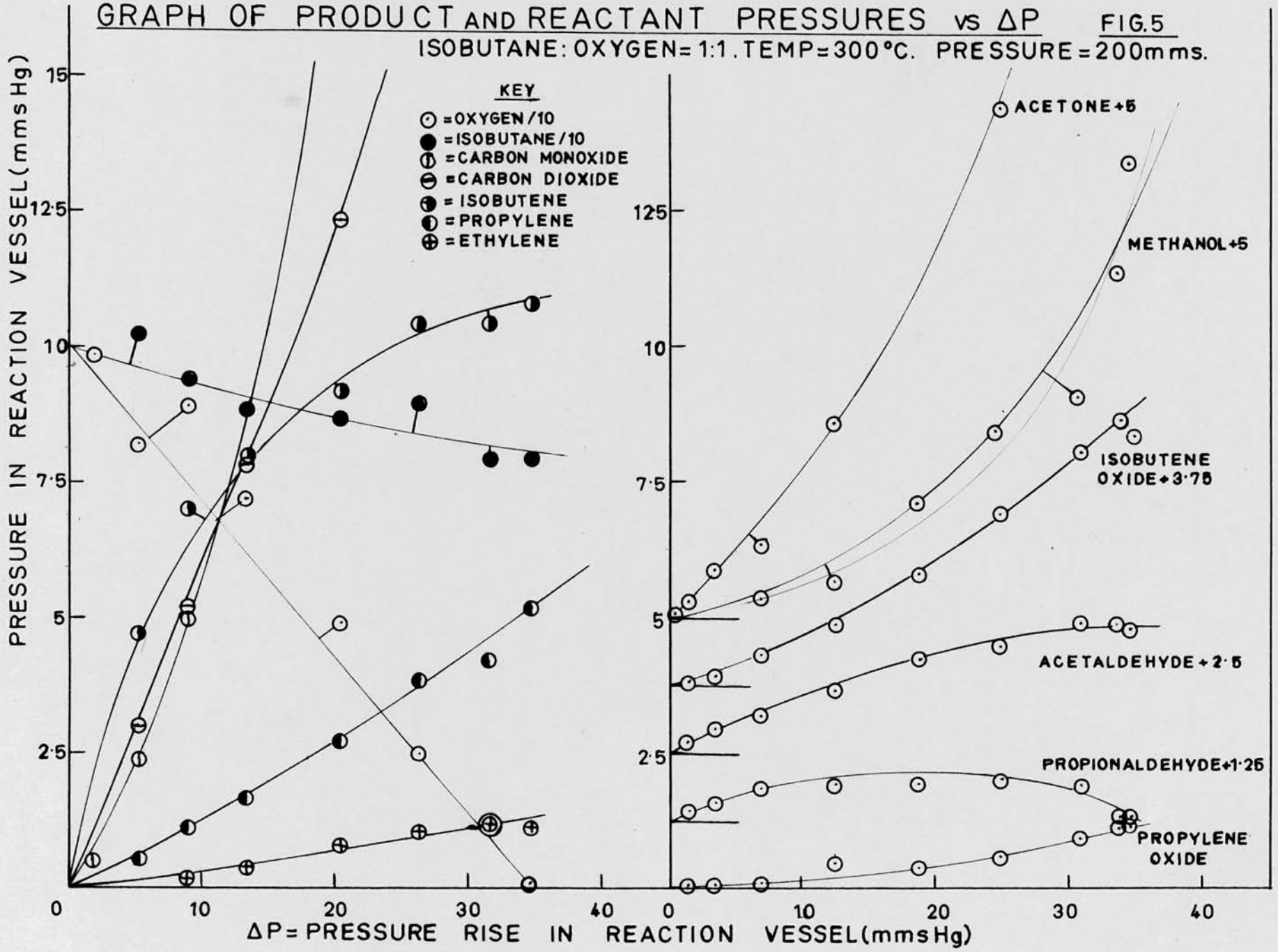
R_s STANDARD RESISTANCE $\sim 10^9 \Omega$
A AMPLIFIER
R RECORDER

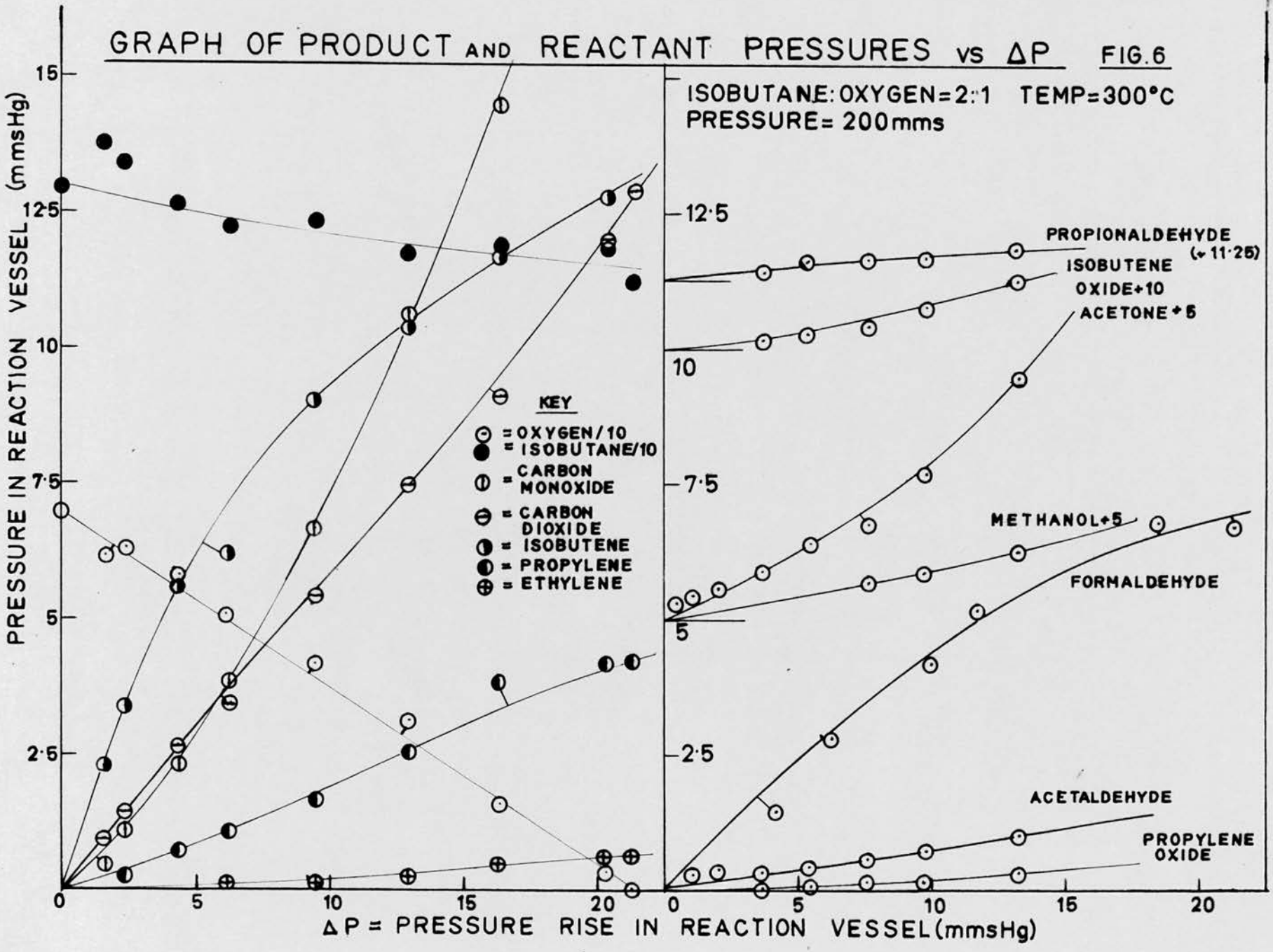
DETECTOR CIRCUIT

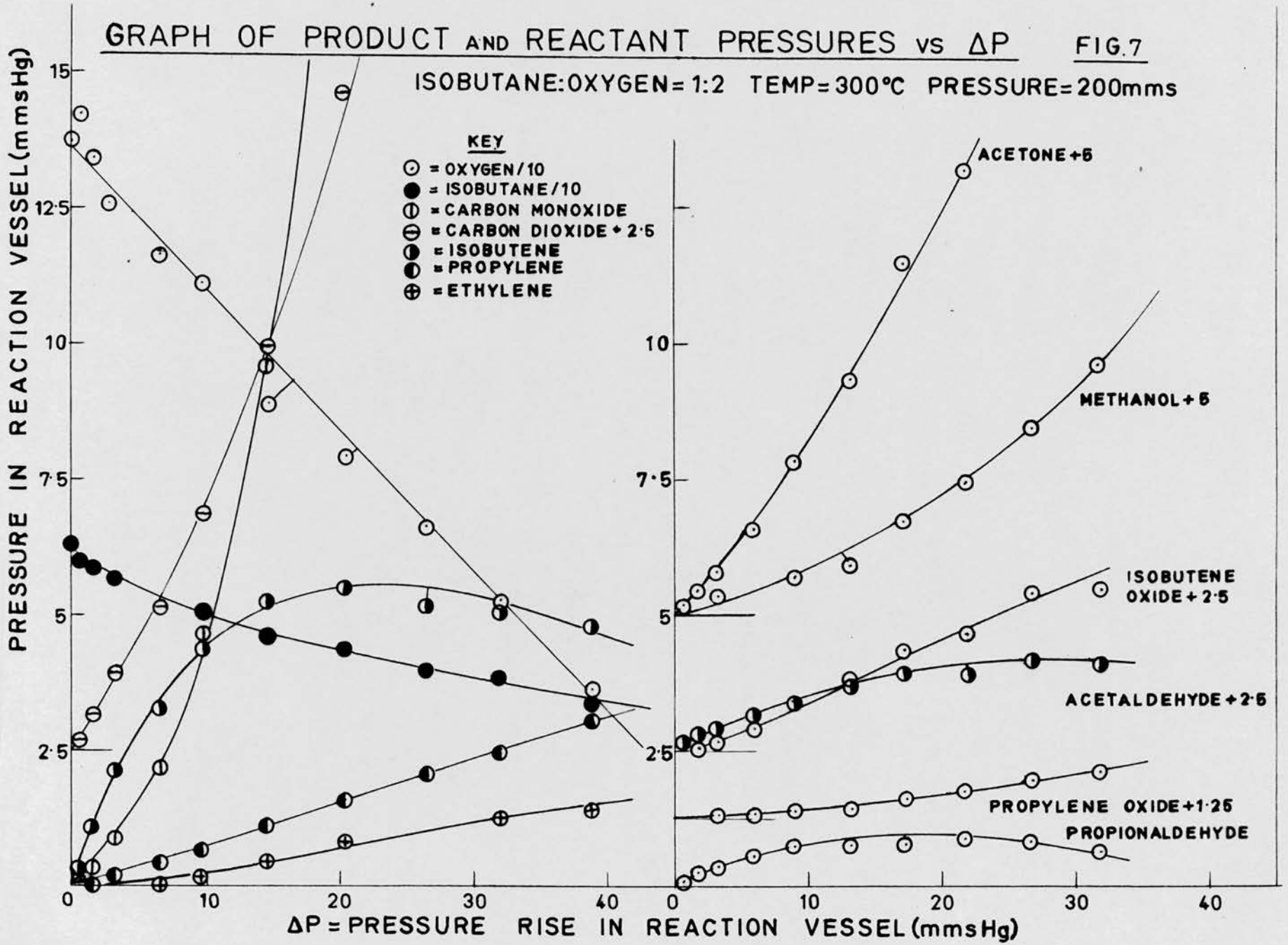


I AMMETER
R 1-10mV. RECORDER

KATHAROMETER CIRCUIT

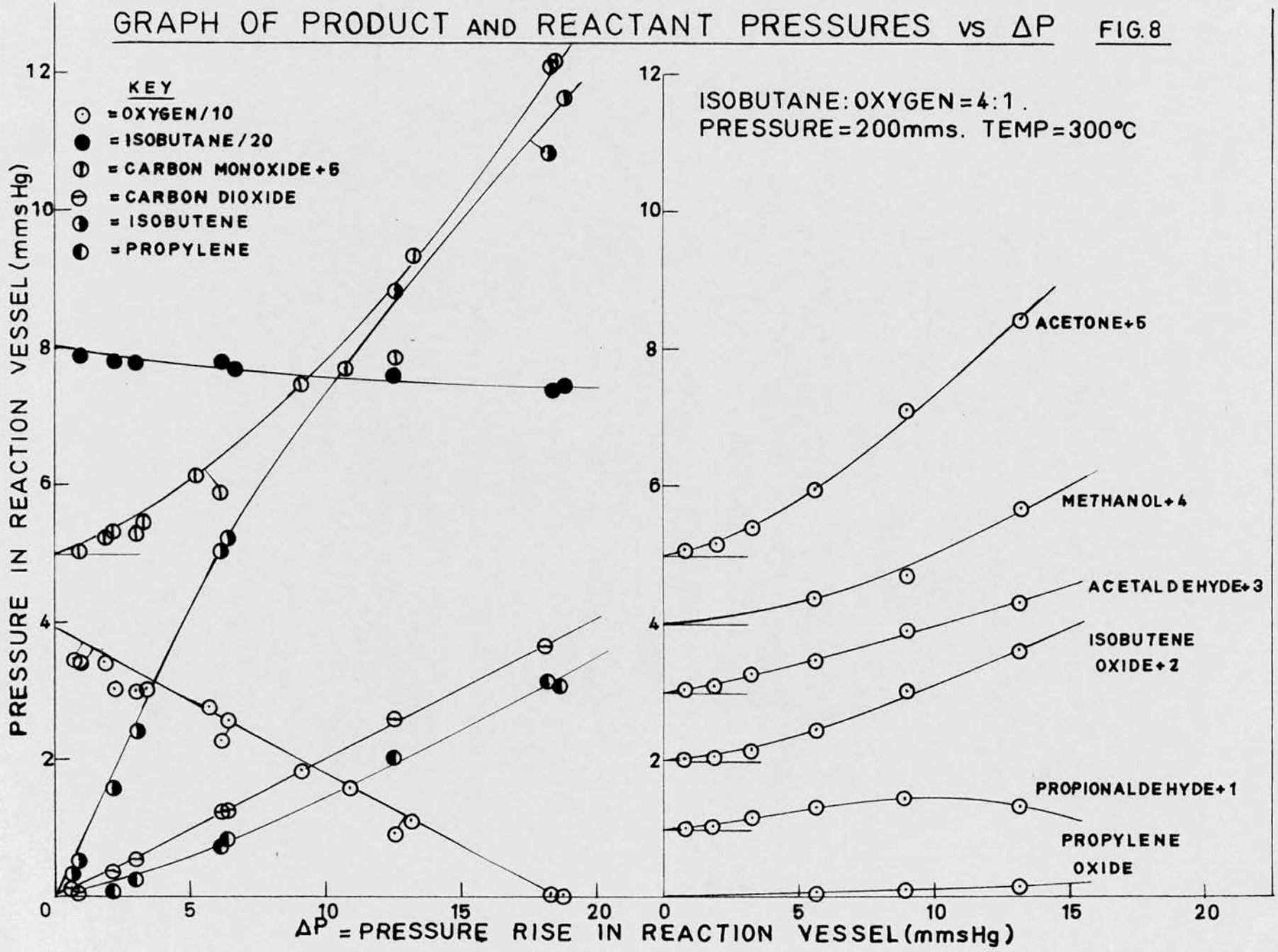

GRAPH OF PRODUCT AND REACTANT PRESSURES vs ΔP
FIG.5
ISOBUTANE: OXYGEN = 1:1. TEMP = 300°C. PRESSURE = 200mms.
KEY
⊙ = OXYGEN/10
● = ISOBUTANE/10
◐ = CARBON MONOXIDE
⊖ = CARBON DIOXIDE
◑ = ISOBUTENE
◐ = PROPYLENE
⊕ = ETHYLENE
ACETONE+5
METHANOL+5
ISOBUTENE OXIDE+3·75
ACETALDEHYDE+2·5
PROPIONALDEHYDE+1·25
PROPYLENE OXIDE
PRESSURE IN REACTION VESSEL (mms Hg)
ΔP = PRESSURE RISE IN REACTION VESSEL (mms Hg)
0
10
20
30
40
2·5
5
7·5
10
12·5
15
125

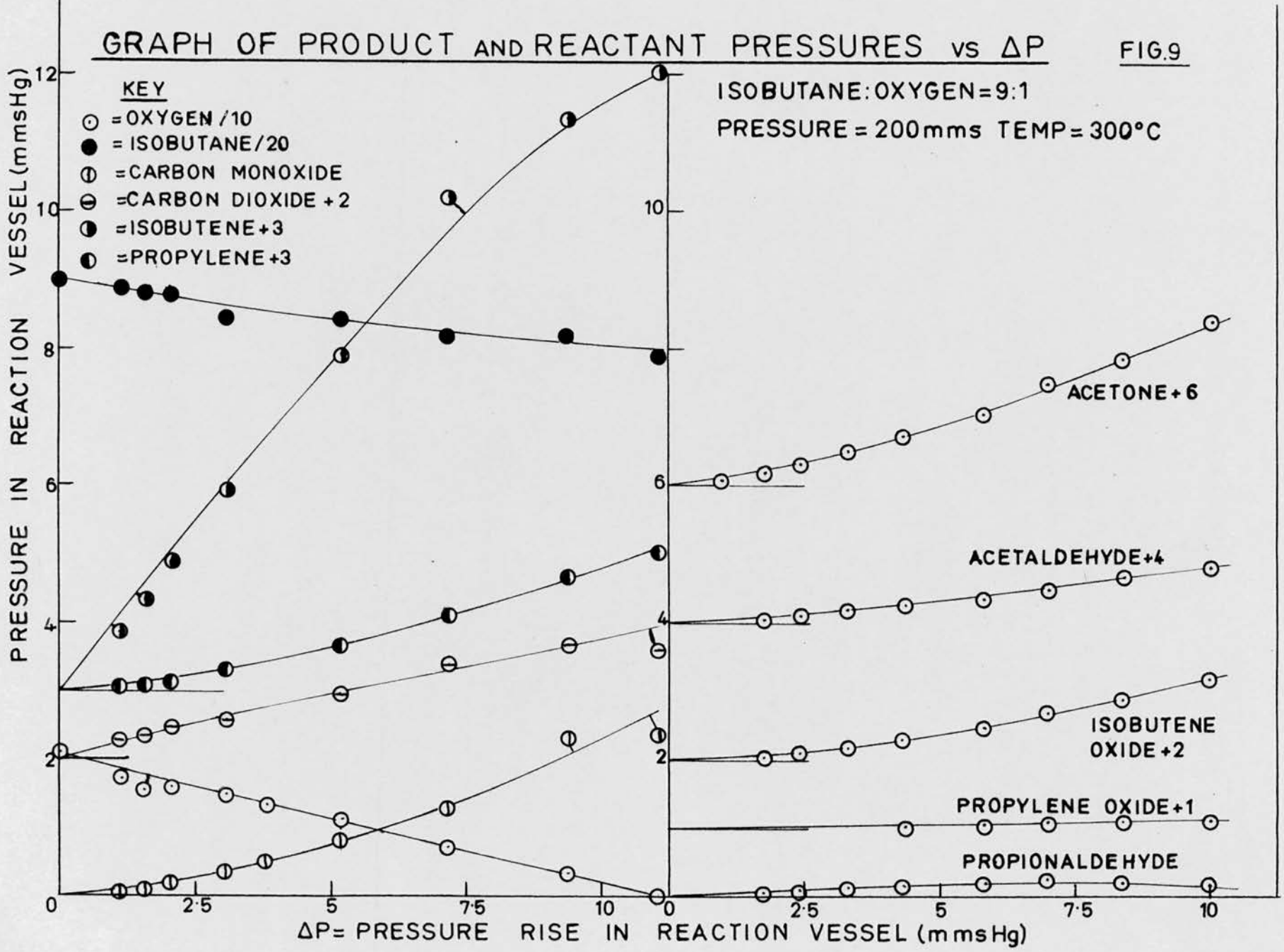

GRAPH OF PRODUCT AND REACTANT PRESSURES vs ΔP
FIG.6
ISOBUTANE: OXYGEN = 2:1 TEMP = 300°C
PRESSURE = 200 mms
PRESSURE IN REACTION VESSEL (mmsHg)
ΔP = PRESSURE RISE IN REACTION VESSEL (mmsHg)
KEY
= OXYGEN/10
= ISOBUTANE/10
= CARBON MONOXIDE
= CARBON DIOXIDE
= ISOBUTENE
= PROPYLENE
= ETHYLENE
PROPIONALDEHYDE (+11·25)
ISOBUTENE OXIDE+10
ACETONE+5
METHANOL+5
FORMALDEHYDE
ACETALDEHYDE
PROPYLENE OXIDE

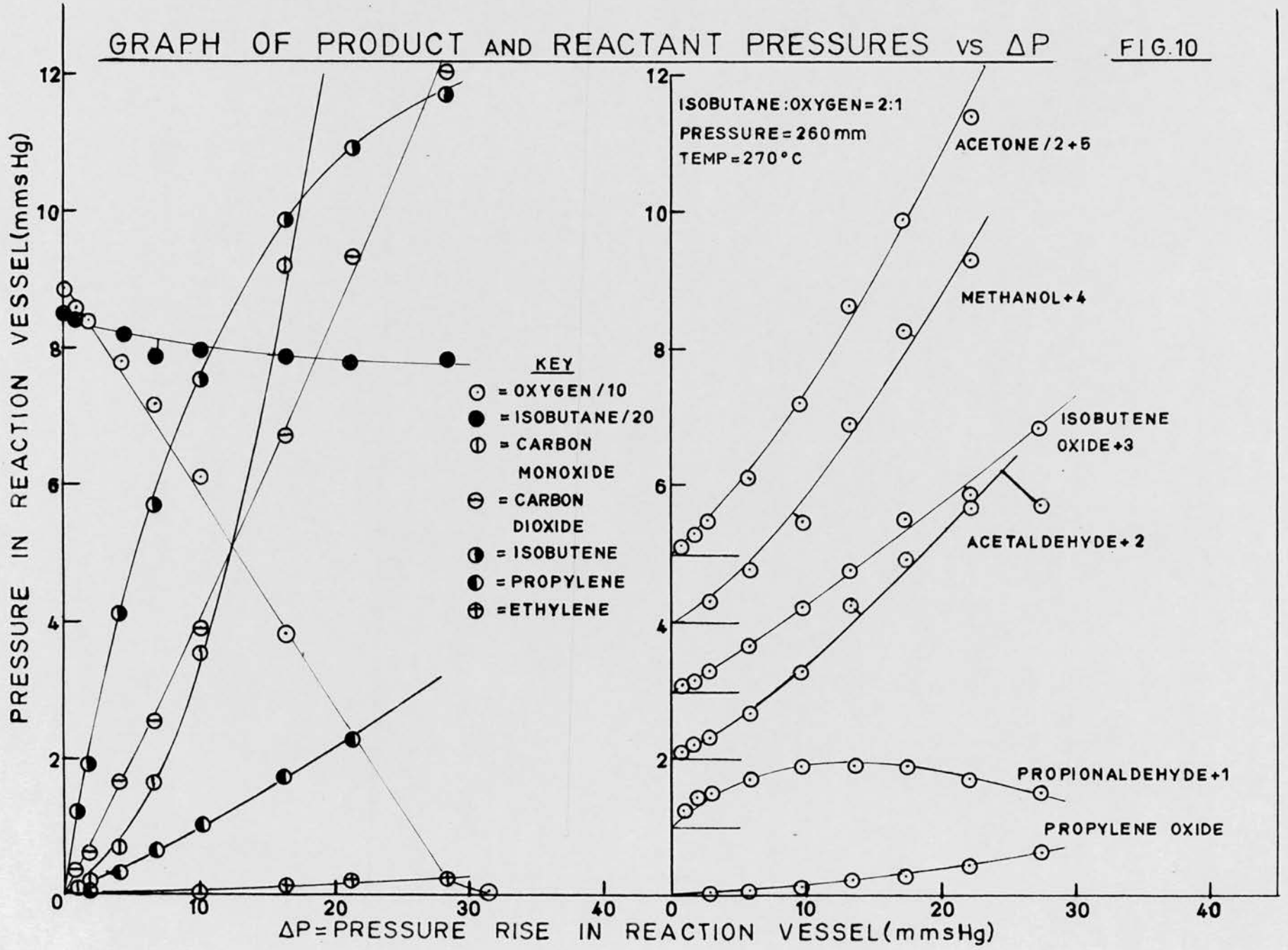

GRAPH OF PRODUCT AND REACTANT PRESSURES vs ΔP
FIG.7
ISOBUTANE:OXYGEN = 1:2 TEMP = 300°C PRESSURE = 200mms
KEY
⊙ = OXYGEN/10
● = ISOBUTANE/10
⊖ = CARBON MONOXIDE
⊖ = CARBON DIOXIDE + 2·5
◑ = ISOBUTENE
◐ = PROPYLENE
⊕ = ETHYLENE
ACETONE+5
METHANOL+5
ISOBUTENE OXIDE+2·5
ACETALDEHYDE+2·5
PROPYLENE OXIDE+1·25
PROPIONALDEHYDE
PRESSURE IN REACTION VESSEL (mmsHg)
ΔP = PRESSURE RISE IN REACTION VESSEL (mmsHg)
15
12·5
10
7·5
5
2·5
0
10
20
30
40

GRAPH OF PRODUCT AND REACTANT PRESSURES vs ΔP

FIG.8




GRAPH OF PRODUCT AND REACTANT PRESSURES vs ΔP
FIG.9
KEY
⊙ = OXYGEN /10
● = ISOBUTANE/20
⊖ = CARBON MONOXIDE
⊖ = CARBON DIOXIDE + 2
◑ = ISOBUTENE + 3
◐ = PROPYLENE + 3
ISOBUTANE:OXYGEN = 9:1
PRESSURE = 200 mms TEMP = 300°C
ACETONE + 6
ACETALDEHYDE + 4
ISOBUTENE OXIDE + 2
PROPYLENE OXIDE + 1
PROPIONALDEHYDE
PRESSURE IN REACTION VESSEL (mmsHg)
ΔP = PRESSURE RISE IN REACTION VESSEL (mms Hg)
0
2·5
5
7·5
10
2
4
6
8
10
12


GRAPH OF PRODUCT AND REACTANT PRESSURES vs ΔP
FIG.10
ISOBUTANE:OXYGEN=2:1
PRESSURE=260mm
TEMP=270°C
KEY
= OXYGEN/10
= ISOBUTANE/20
= CARBON MONOXIDE
= CARBON DIOXIDE
= ISOBUTENE
= PROPYLENE
= ETHYLENE
ACETONE/2+5
METHANOL+4
ISOBUTENE OXIDE+3
ACETALDEHYDE+2
PROPIONALDEHYDE+1
PROPYLENE OXIDE
PRESSURE IN REACTION VESSEL(mmsHg)
ΔP=PRESSURE RISE IN REACTION VESSEL(mmsHg)
0
2
4
6
8
10
12
10
20
30
40

GRAPH OF PRODUCT AND REACTANT PRESSURES vs ΔP FIG.11

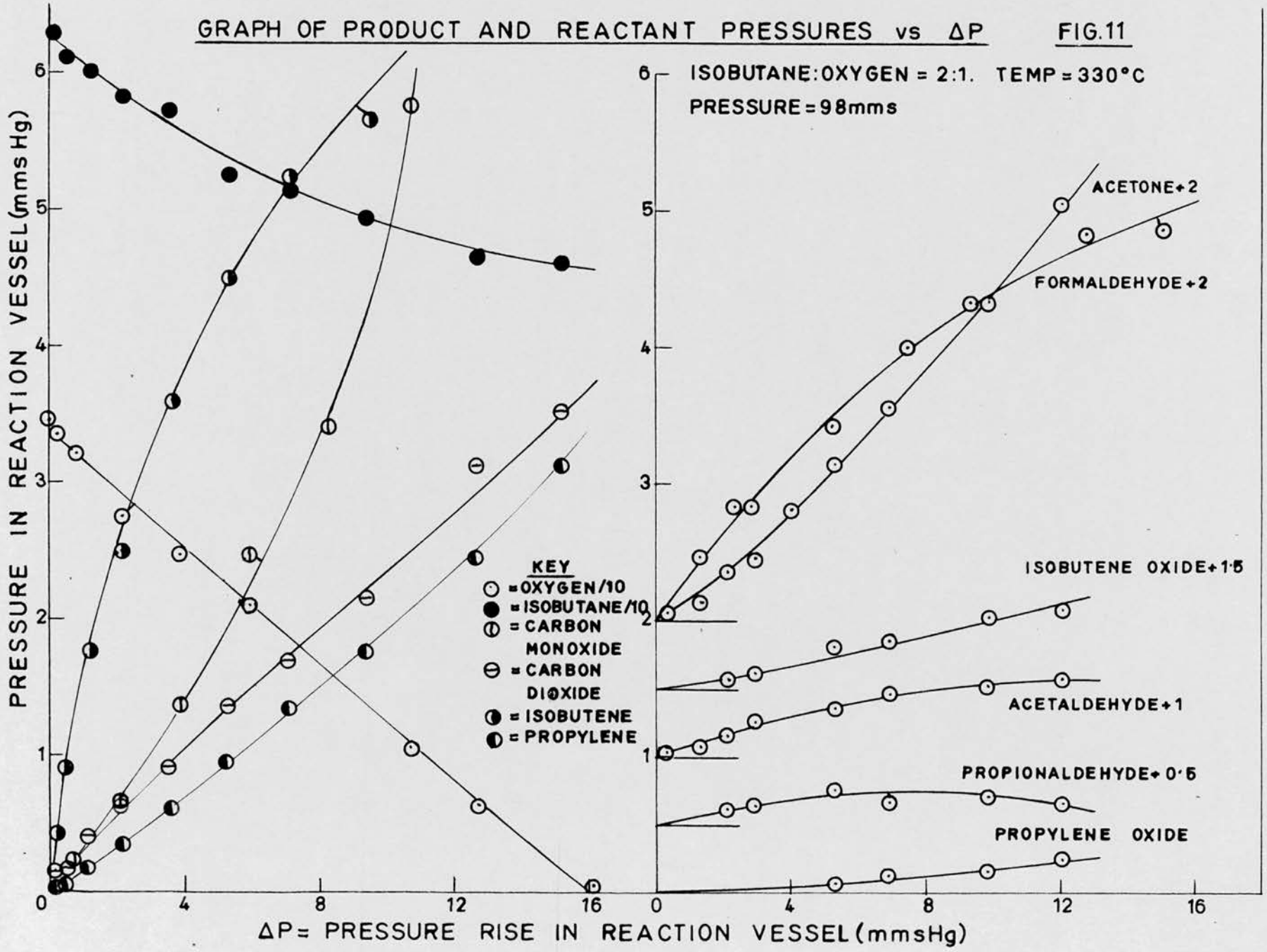


FIG.12

GRAPH OF PRODUCT AND REACTANT PRESSURES vs ΔP

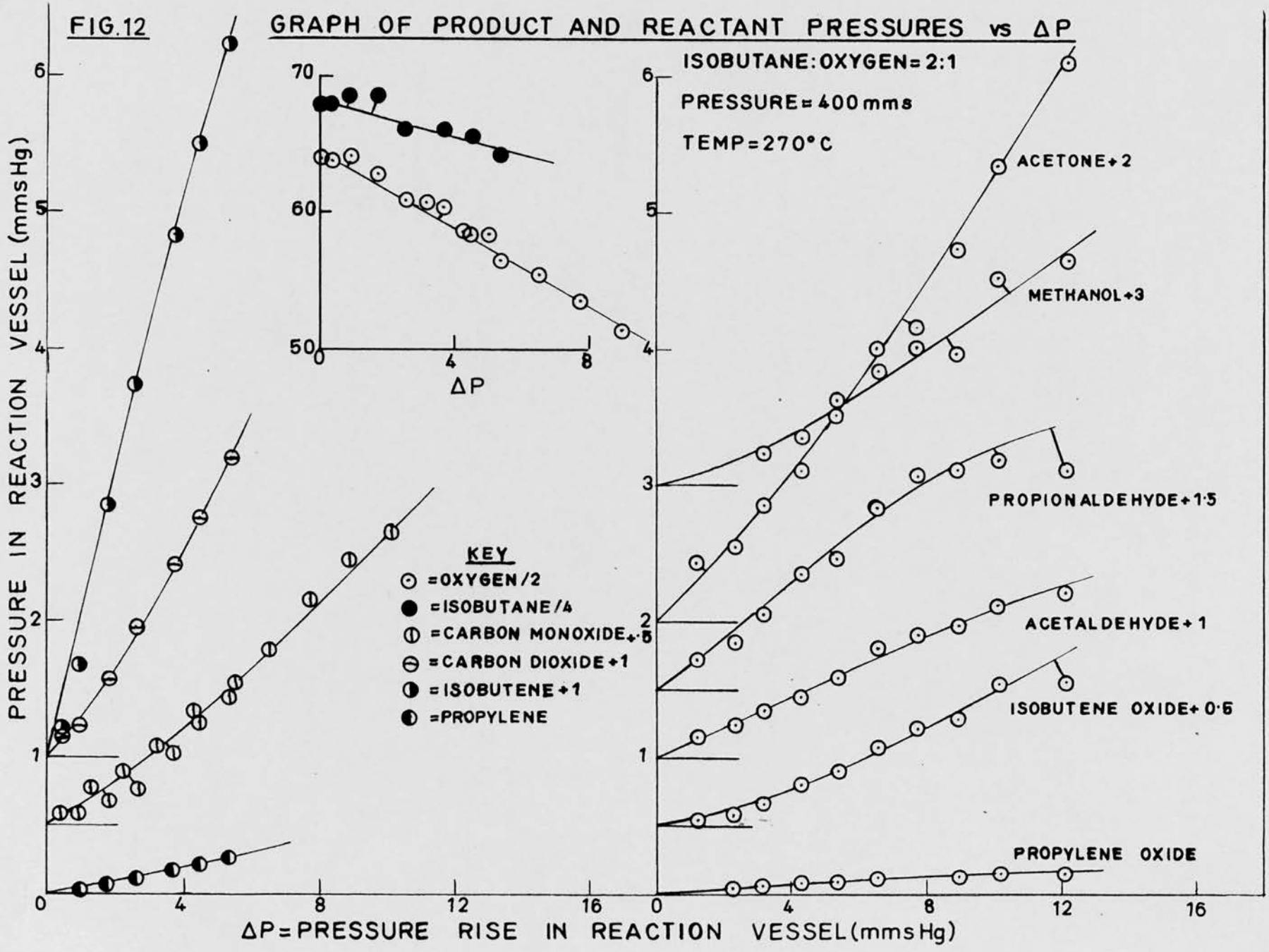


FIG. 13

GRAPH OF OXYGEN PRESSURE vs PRESSURE RISE

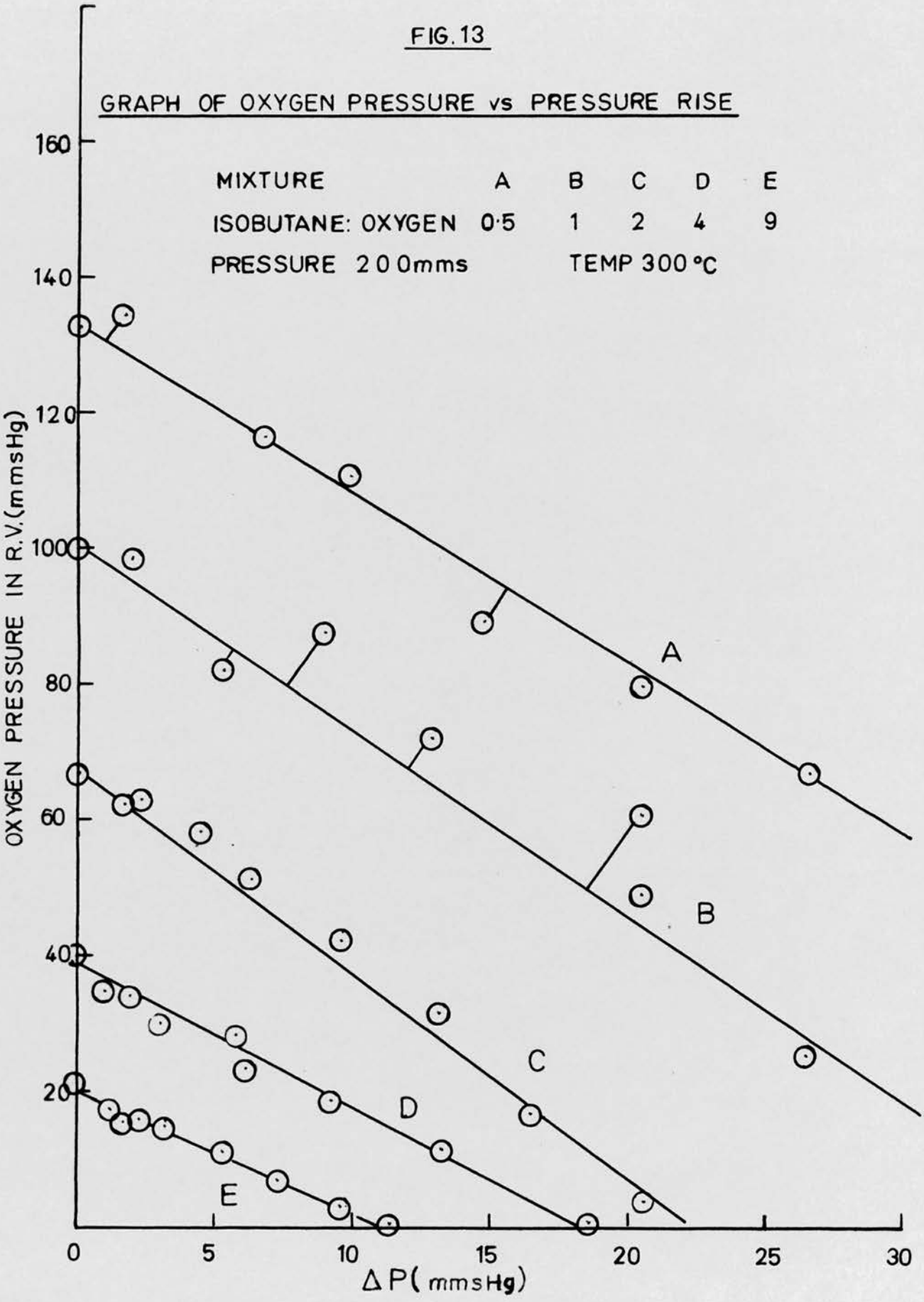


FIG. 14

GRAPH OF OXYGEN PRESSURE vs mm ATOMS CARBON IN TOTAL PRODUCT

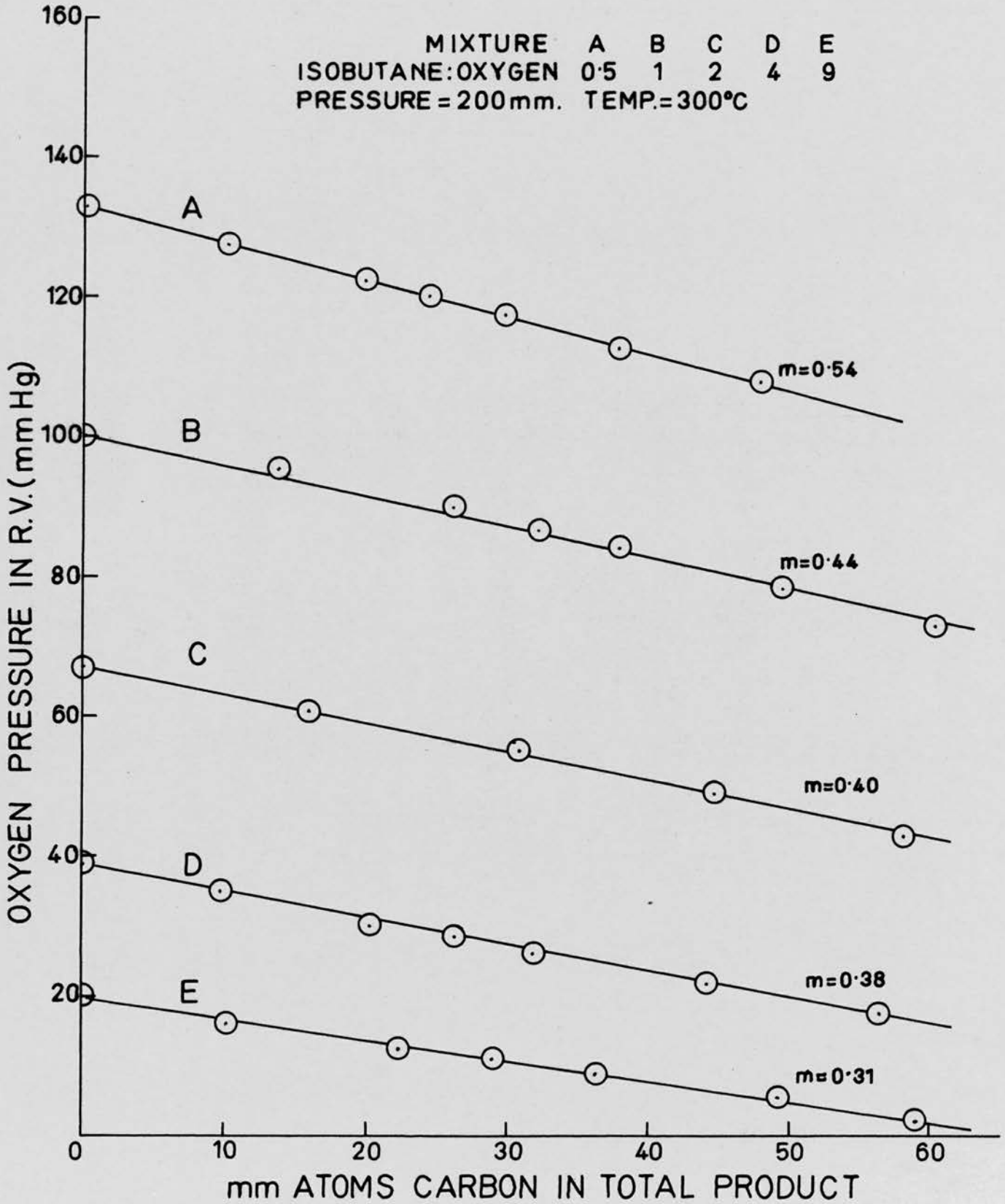
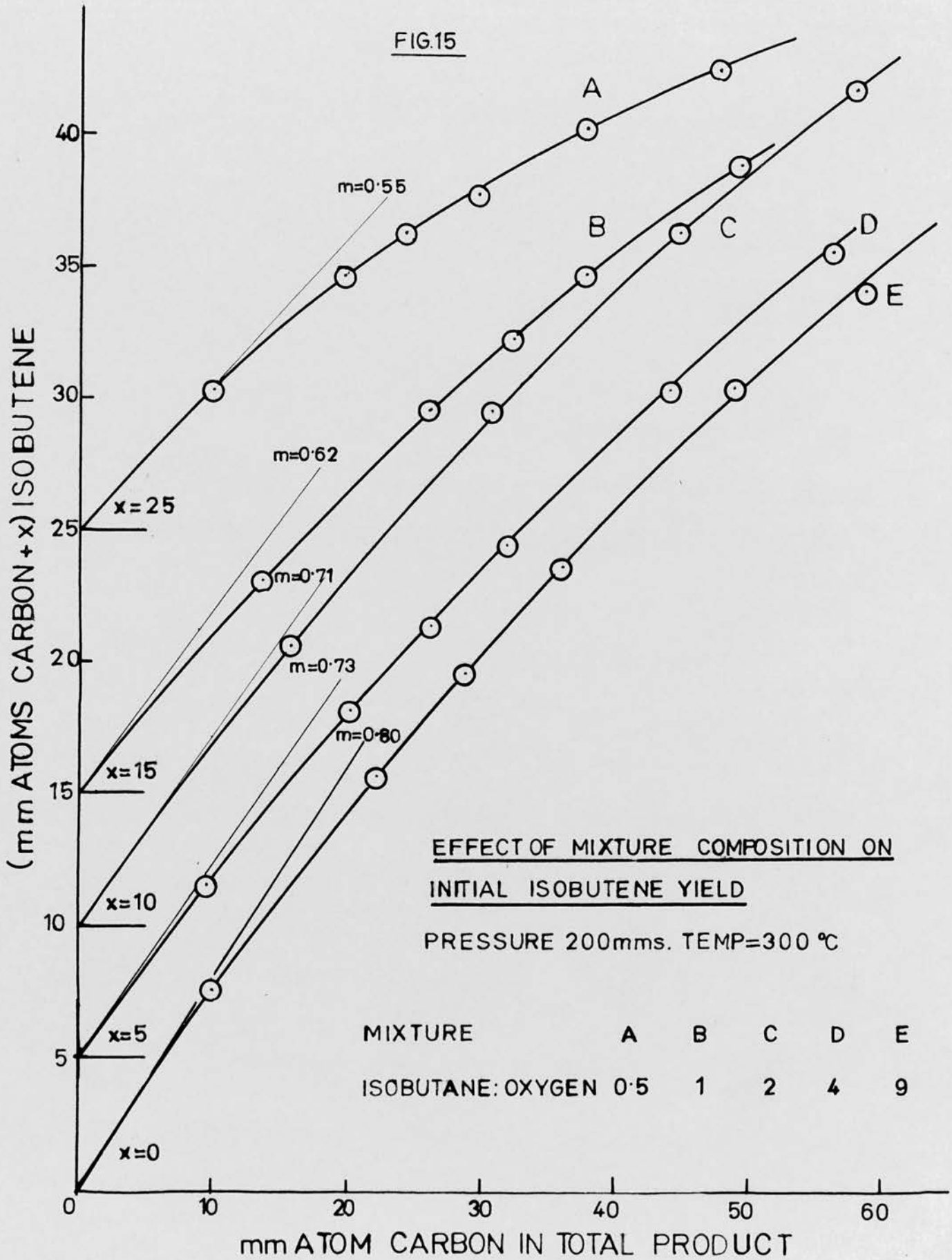


FIG.15



EFFECT OF MIXTURE COMPOSITION ON INITIAL ISOBUTENE YIELD

PRESSURE 200mms. TEMP=300 °C

MIXTURE	A	B	C	D	E
ISOBUTANE: OXYGEN	0·5	1	2	4	9

FIG. 16

EFFECT OF MIXTURE COMPOSITION ON INITIAL ACETONE YIELD

PRESSURE 200 mms. TEMP. 300 °C

MIXTURE	ISOBUTANE / OXYGEN
A	0·5
B	1·0
C	2·0
D	4·0
E	9·0

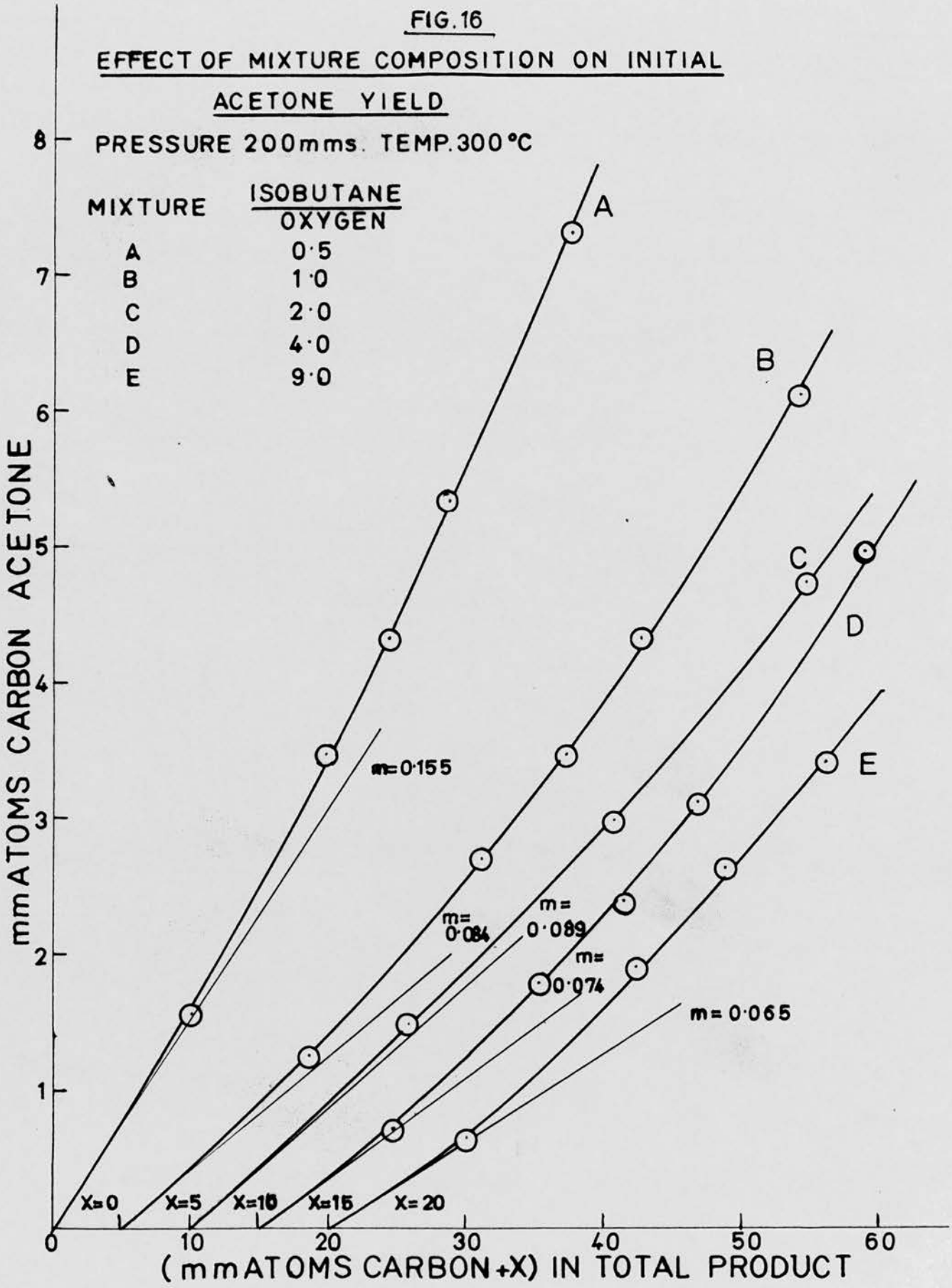
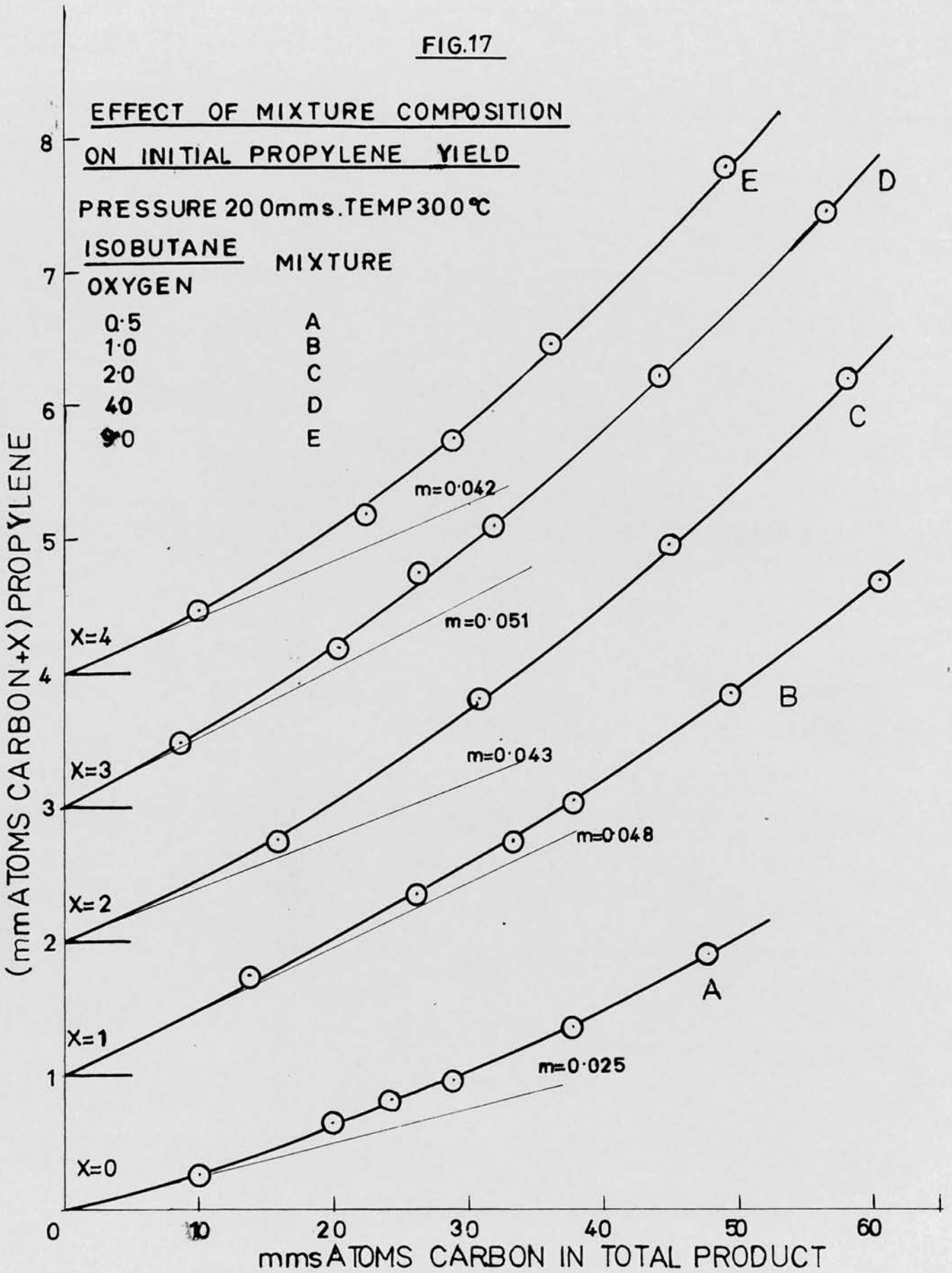


FIG.17


EFFECT OF MIXTURE COMPOSITION
ON INITIAL PROPYLENE YIELD
PRESSURE 200mms. TEMP 300°C
ISOBUTANE / OXYGEN MIXTURE
0·5 A
1·0 B
2·0 C
4·0 D
9·0 E
(mmATOMS CARBON+X) PROPYLENE
mmsATOMS CARBON IN TOTAL PRODUCT
X=0
X=1
X=2
X=3
X=4
m=0·025
m=0·048
m=0·043
m=0·051
m=0·042
A
B
C
D
E
0
10
20
30
40
50
60
1
2
3
4
5
6
7
8

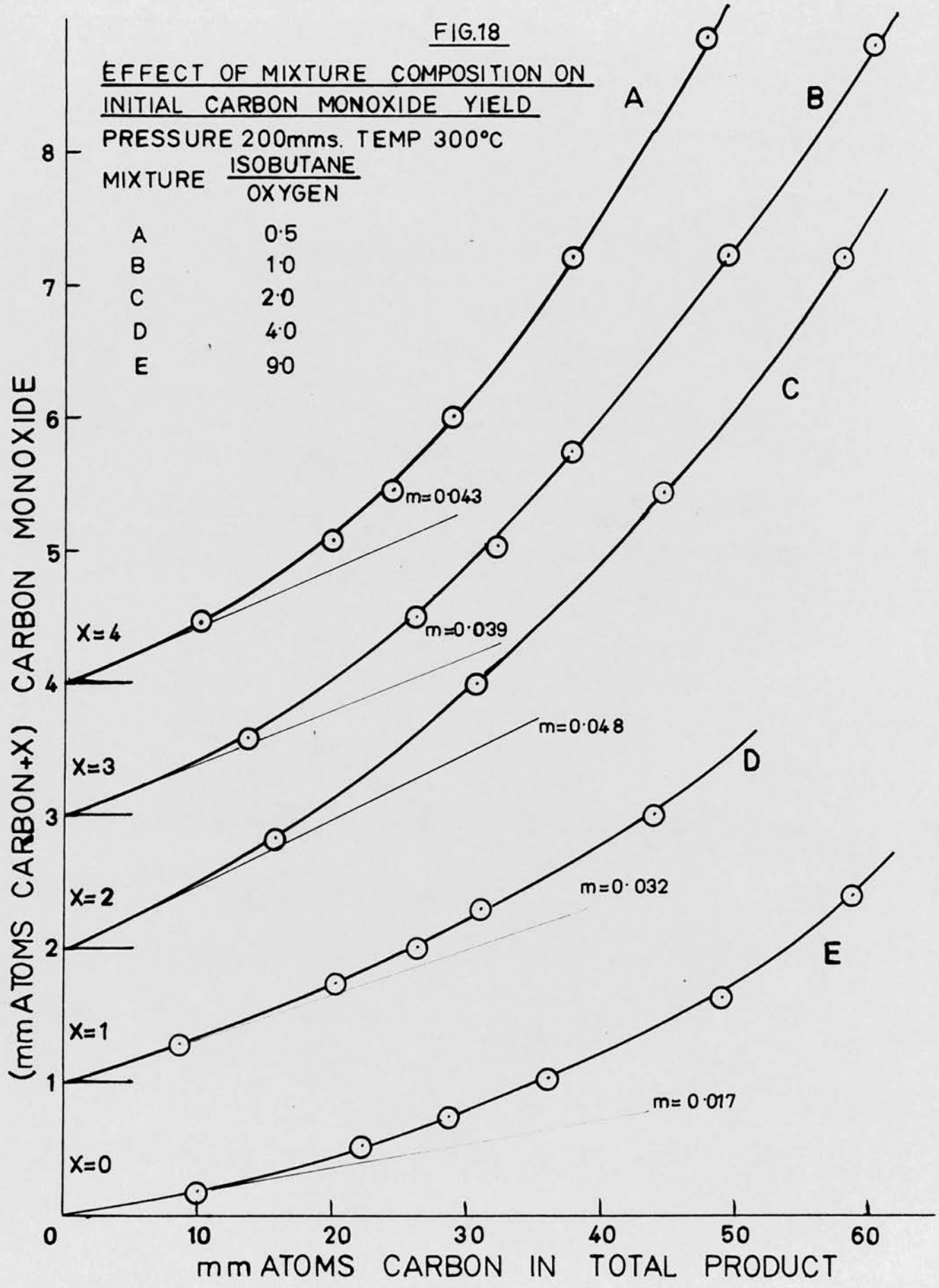


FIG.18
EFFECT OF MIXTURE COMPOSITION ON INITIAL CARBON MONOXIDE YIELD
PRESSURE 200mms. TEMP 300°C
MIXTURE ISOBUTANE / OXYGEN
A 0·5
B 1·0
C 2·0
D 4·0
E 9·0
A
B
C
D
E
m=0·043
m=0·039
m=0·048
m=0·032
m=0·017
X=4
X=3
X=2
X=1
X=0
(mm ATOMS CARBON+X) CARBON MONOXIDE
mm ATOMS CARBON IN TOTAL PRODUCT
0
10
20
30
40
50
60
1
2
3
4
5
6
7
8

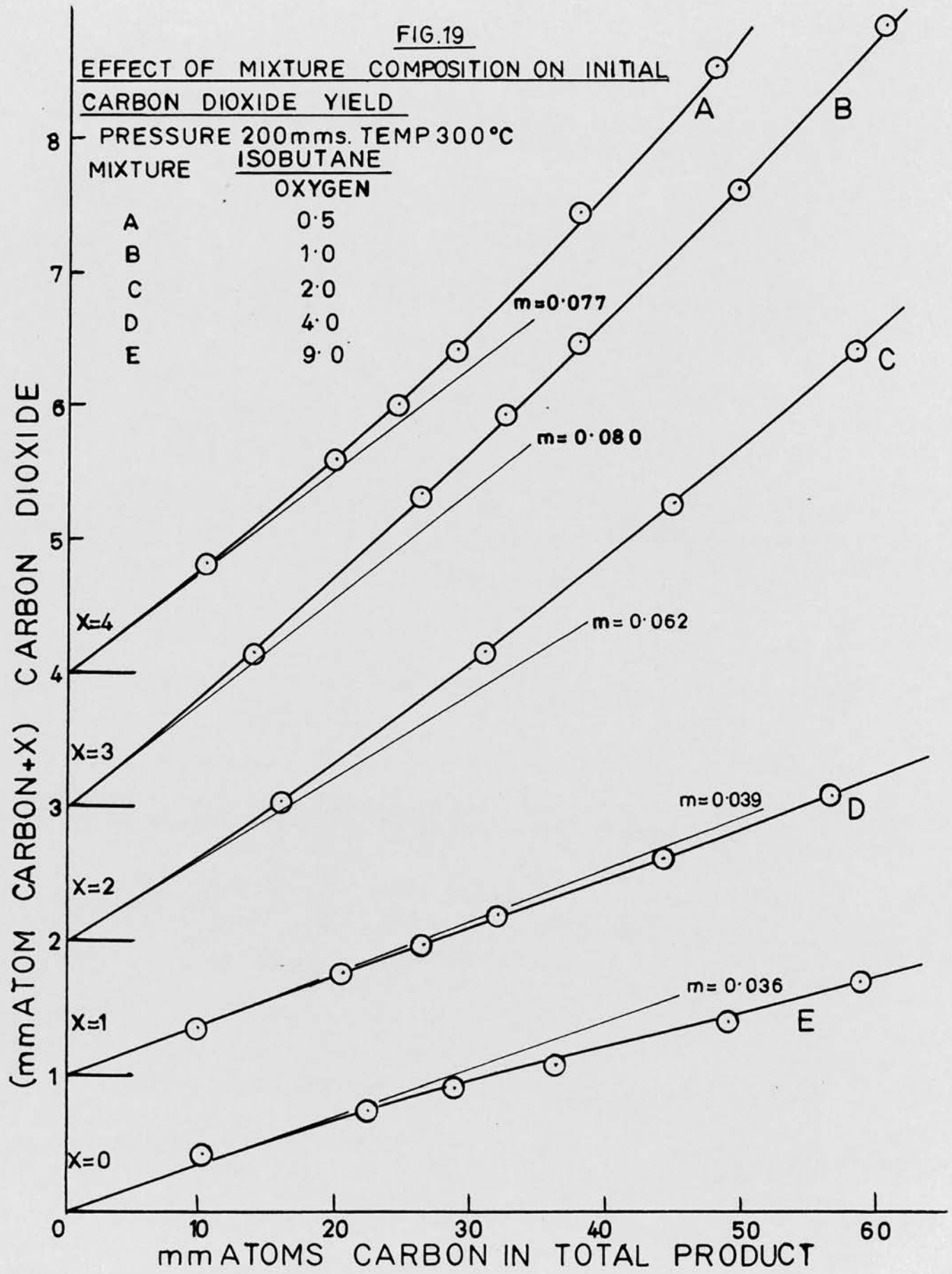


FIG.19
EFFECT OF MIXTURE COMPOSITION ON INITIAL CARBON DIOXIDE YIELD
PRESSURE 200mms. TEMP 300°C
MIXTURE ISOBUTANE / OXYGEN
A 0·5
B 1·0
C 2·0
D 4·0
E 9·0
m=0·077
m= 0·080
m= 0·062
m=0·039
m= 0·036
X=4
X=3
X=2
X=1
X=0
A
B
C
D
E
(mmATOM CARBON+X) CARBON DIOXIDE
mmATOMS CARBON IN TOTAL PRODUCT
0
1
2
3
4
5
6
7
8
10
20
30
40
50
60

FIG. 20

EFFECT OF MIXTURE COMPOSITION ON INITIAL ACETALDEHYDE YIELD

PRESSURE 200 mms. TEMP 300°C

ISOBUTANE: OXYGEN 0·5 1 2 4 9

MIXTURE A B C D E

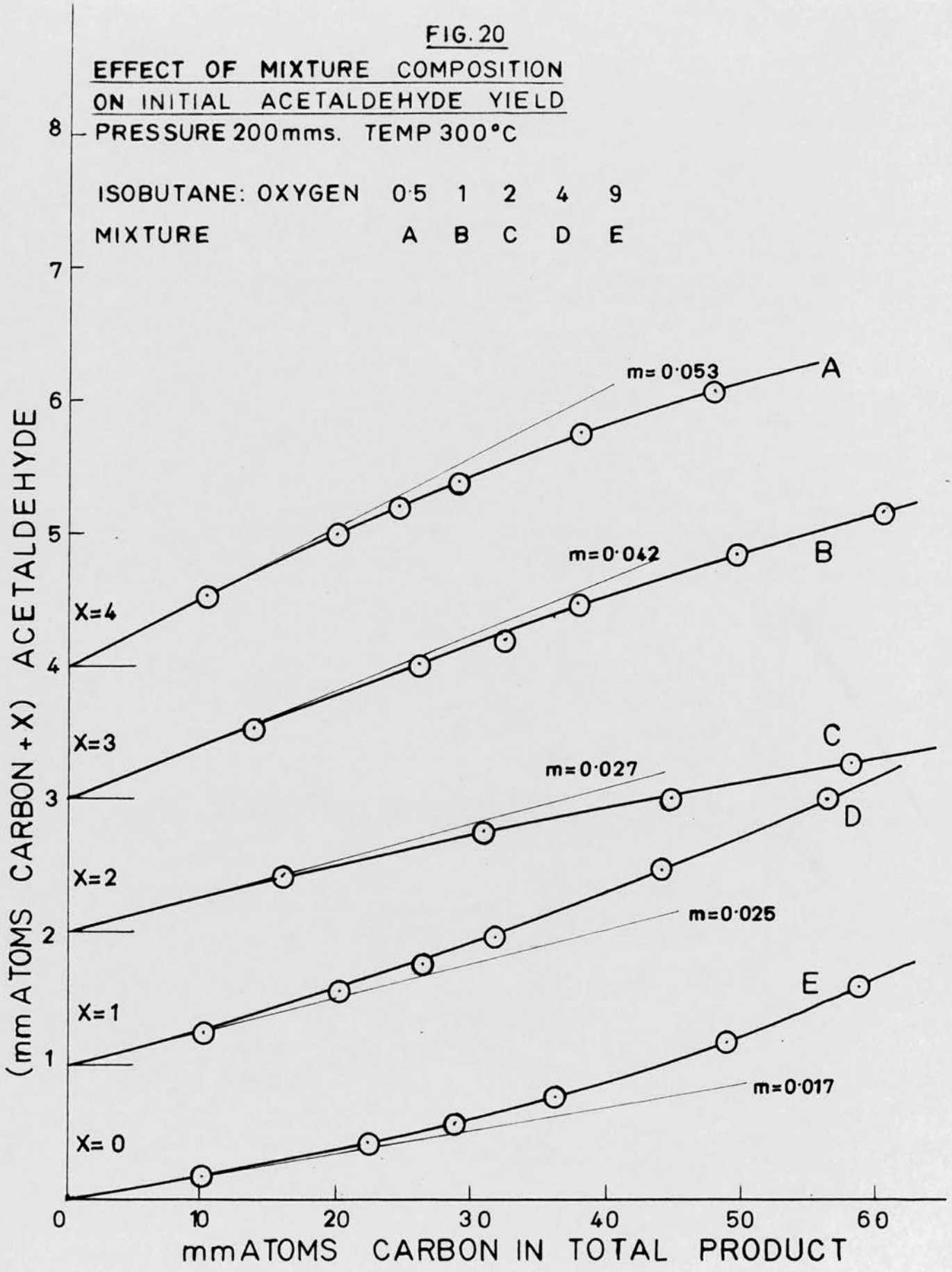
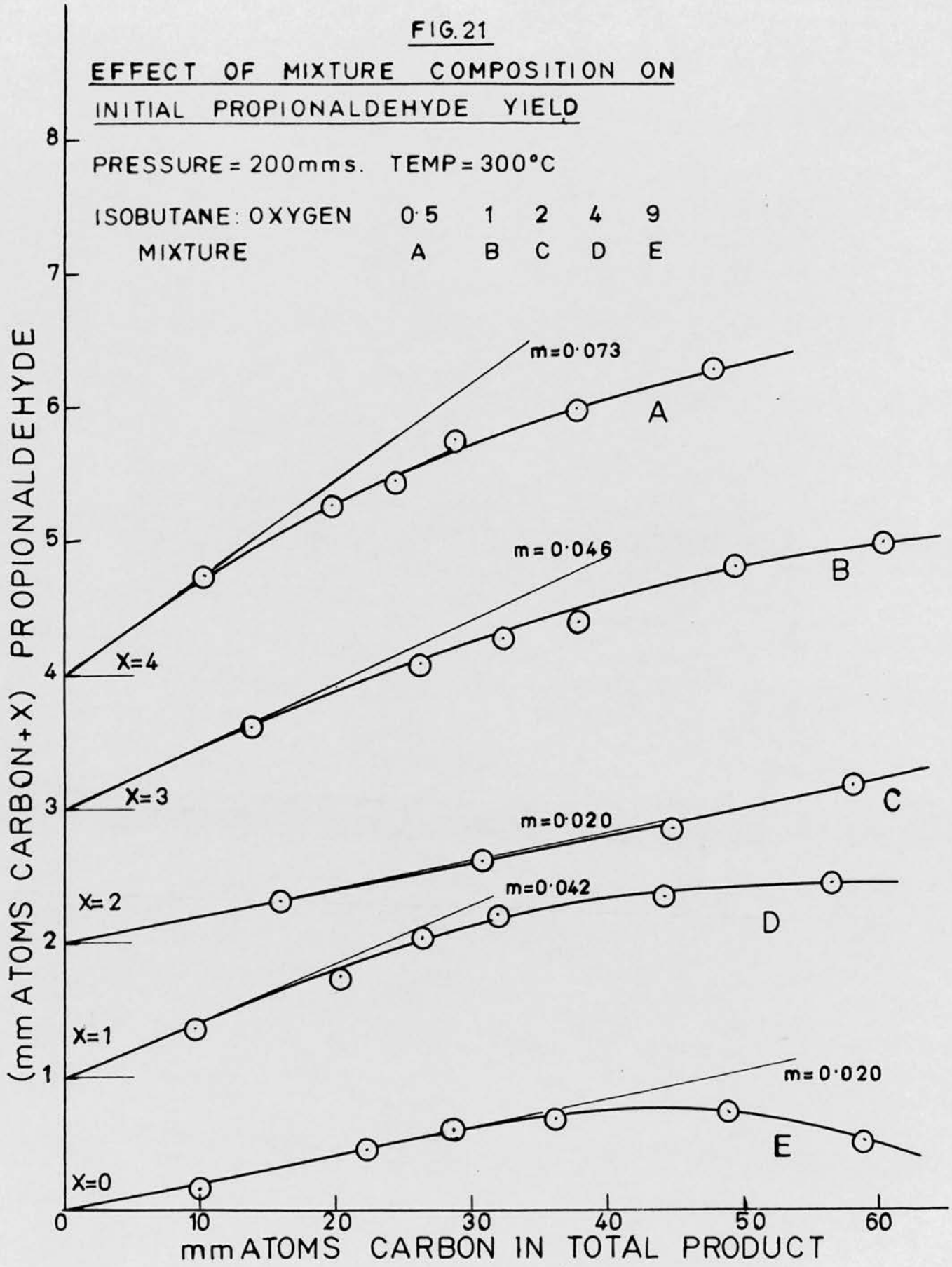


FIG. 21

EFFECT OF MIXTURE COMPOSITION ON INITIAL PROPIONALDEHYDE YIELD



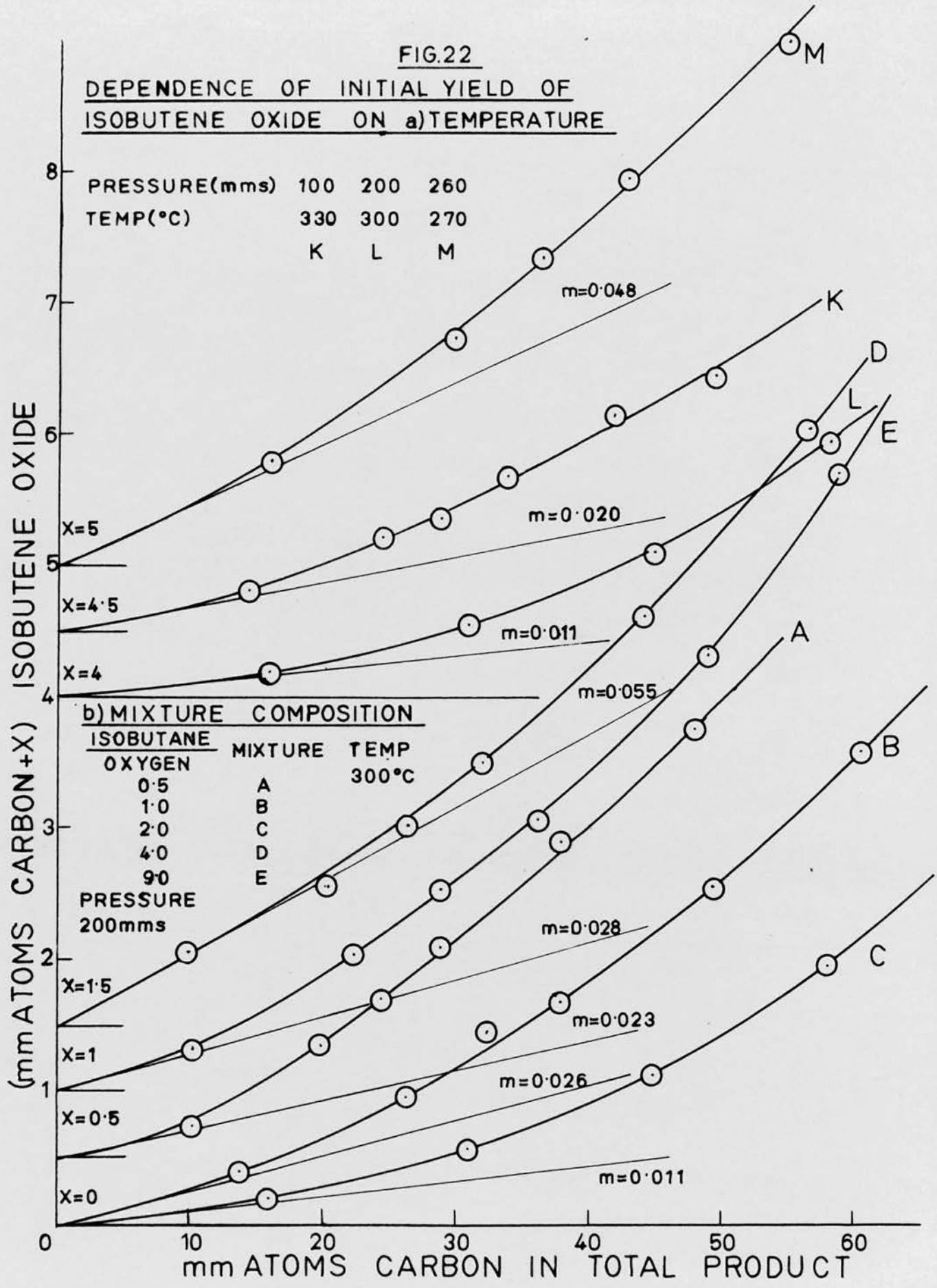
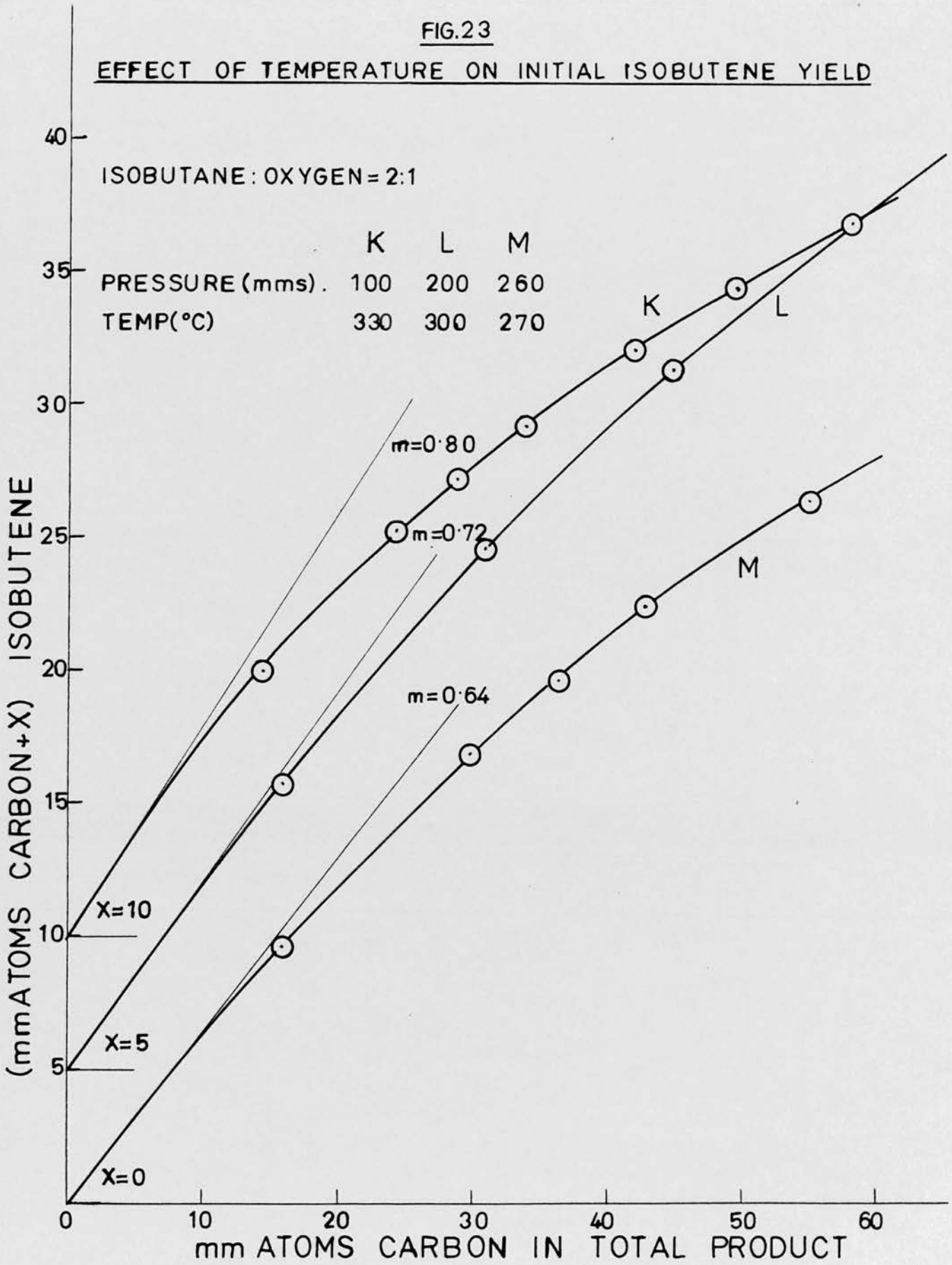


FIG.22
DEPENDENCE OF INITIAL YIELD OF ISOBUTENE OXIDE ON a) TEMPERATURE
PRESSURE(mms) 100 200 260
TEMP(°C) 330 300 270
K L M
b) MIXTURE COMPOSITION
ISOBUTANE / OXYGEN
MIXTURE
TEMP 300°C
0·5 A
1·0 B
2·0 C
4·0 D
9·0 E
PRESSURE 200mms
M
K
D
L
E
A
B
C
m=0·048
m=0·020
m=0·011
m=0·055
m=0·028
m=0·023
m=0·026
m=0·011
X=5
X=4·5
X=4
X=1·5
X=1
X=0·5
X=0
(mm ATOMS CARBON+X) ISOBUTENE OXIDE
mm ATOMS CARBON IN TOTAL PRODUCT
0
1
2
3
4
5
6
7
8
10
20
30
40
50
60

FIG.23

EFFECT OF TEMPERATURE ON INITIAL ISOBUTENE YIELD



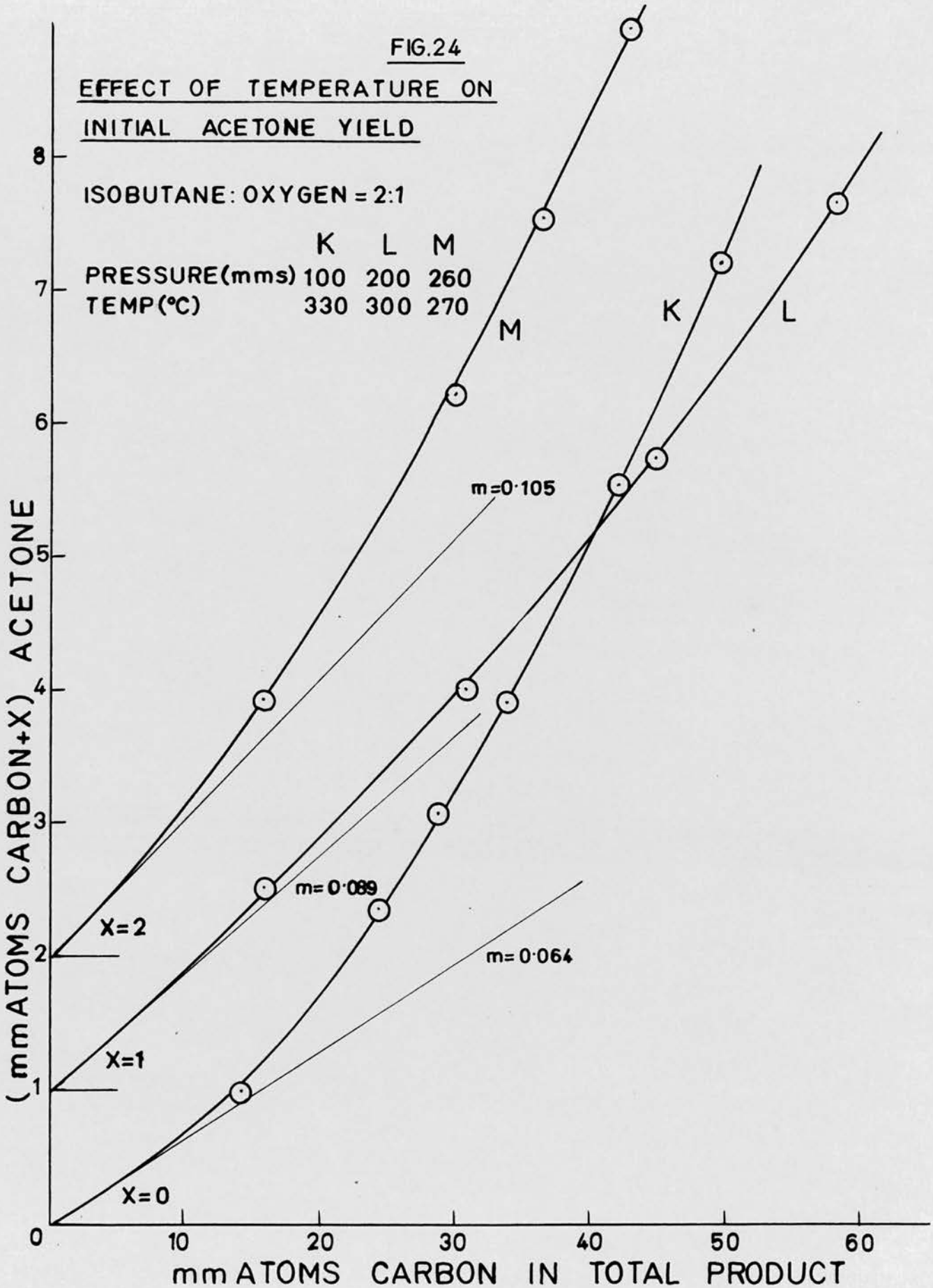
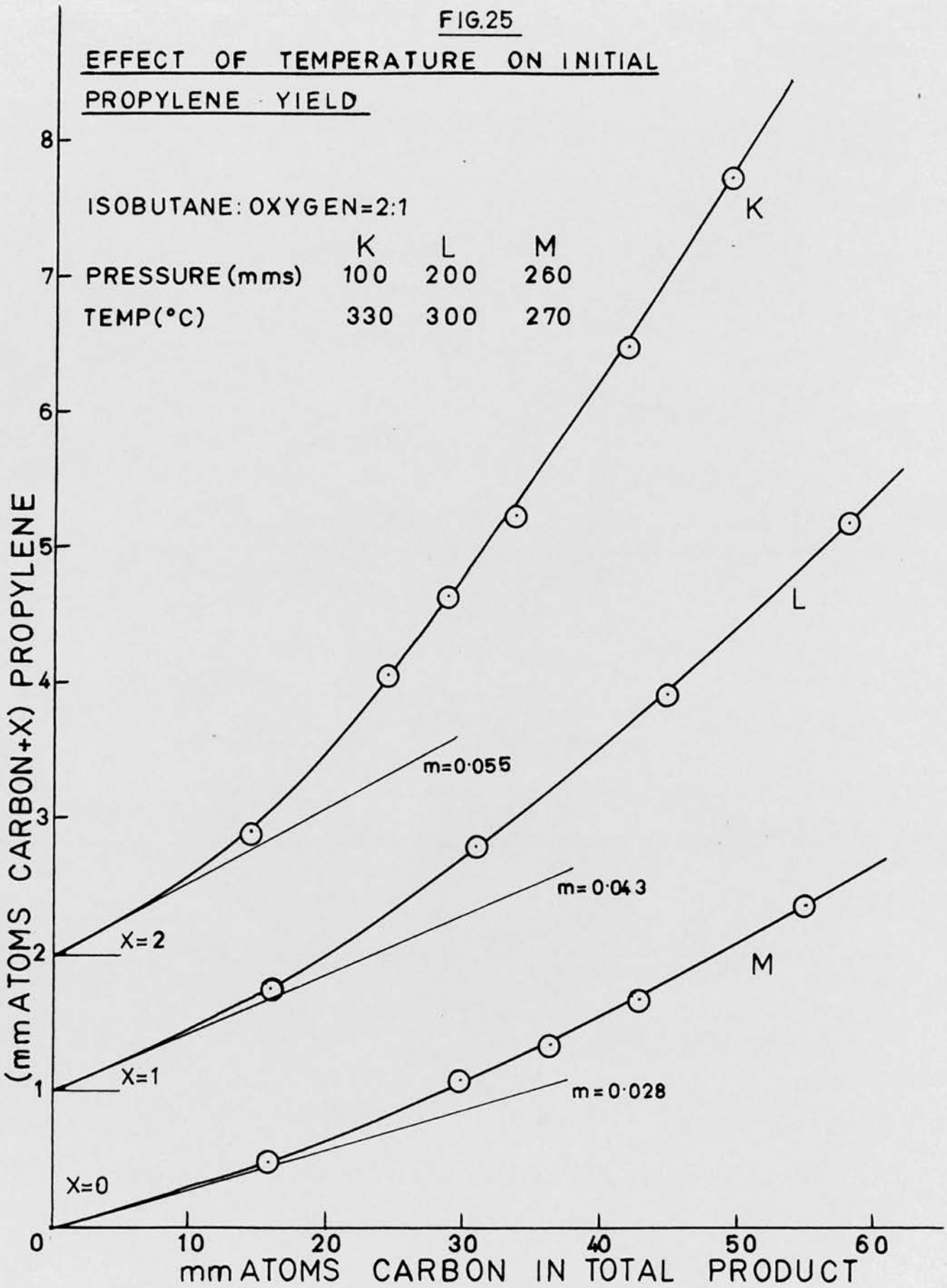


FIG.24
EFFECT OF TEMPERATURE ON INITIAL ACETONE YIELD
ISOBUTANE: OXYGEN = 2:1
K L M
PRESSURE(mms) 100 200 260
TEMP(°C) 330 300 270
M
K
L
m=0·105
m=0·089
m=0·064
X=2
X=1
X=0
(mmATOMS CARBON+X) ACETONE
mmATOMS CARBON IN TOTAL PRODUCT
0
1
2
3
4
5
6
7
8
10
20
30
40
50
60

FIG.25

EFFECT OF TEMPERATURE ON INITIAL PROPYLENE YIELD



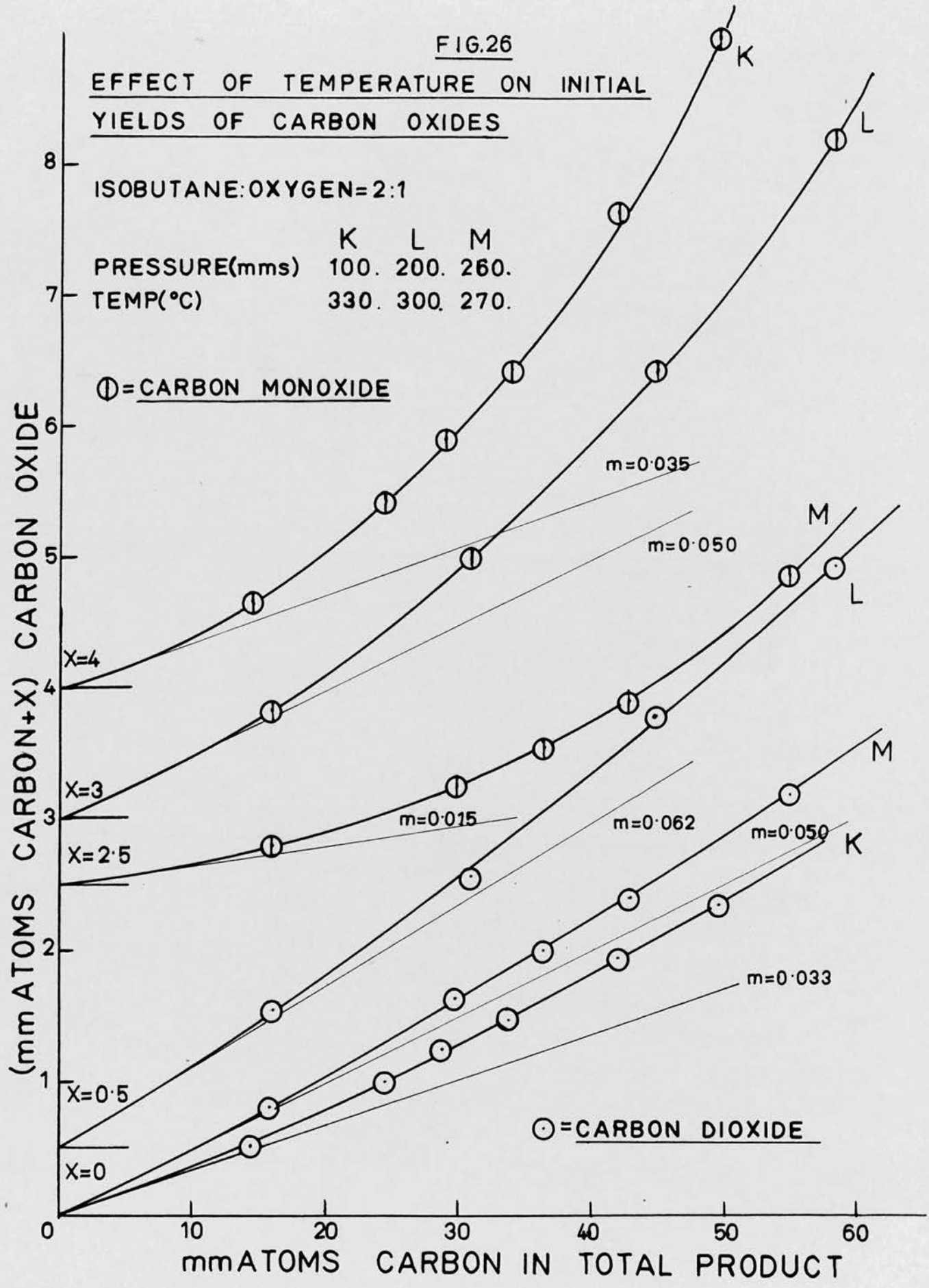


FIG.26
EFFECT OF TEMPERATURE ON INITIAL YIELDS OF CARBON OXIDES
ISOBUTANE:OXYGEN=2:1
K L M
PRESSURE(mms) 100. 200. 260.
TEMP(°C) 330. 300. 270.
⊕=CARBON MONOXIDE
⊙=CARBON DIOXIDE
(mmATOMS CARBON+X) CARBON OXIDE
mmATOMS CARBON IN TOTAL PRODUCT
X=4
X=3
X=2·5
X=0·5
X=0
m=0·035
m=0·050
m=0·015
m=0·062
m=0·050
m=0·033
K
L
M
L
M
K
0
10
20
30
40
50
60
1
2
3
4
5
6
7
8

FIG. 27

EFFECT OF TEMPERATURE ON INITIAL ALDEHYDE YIELDS

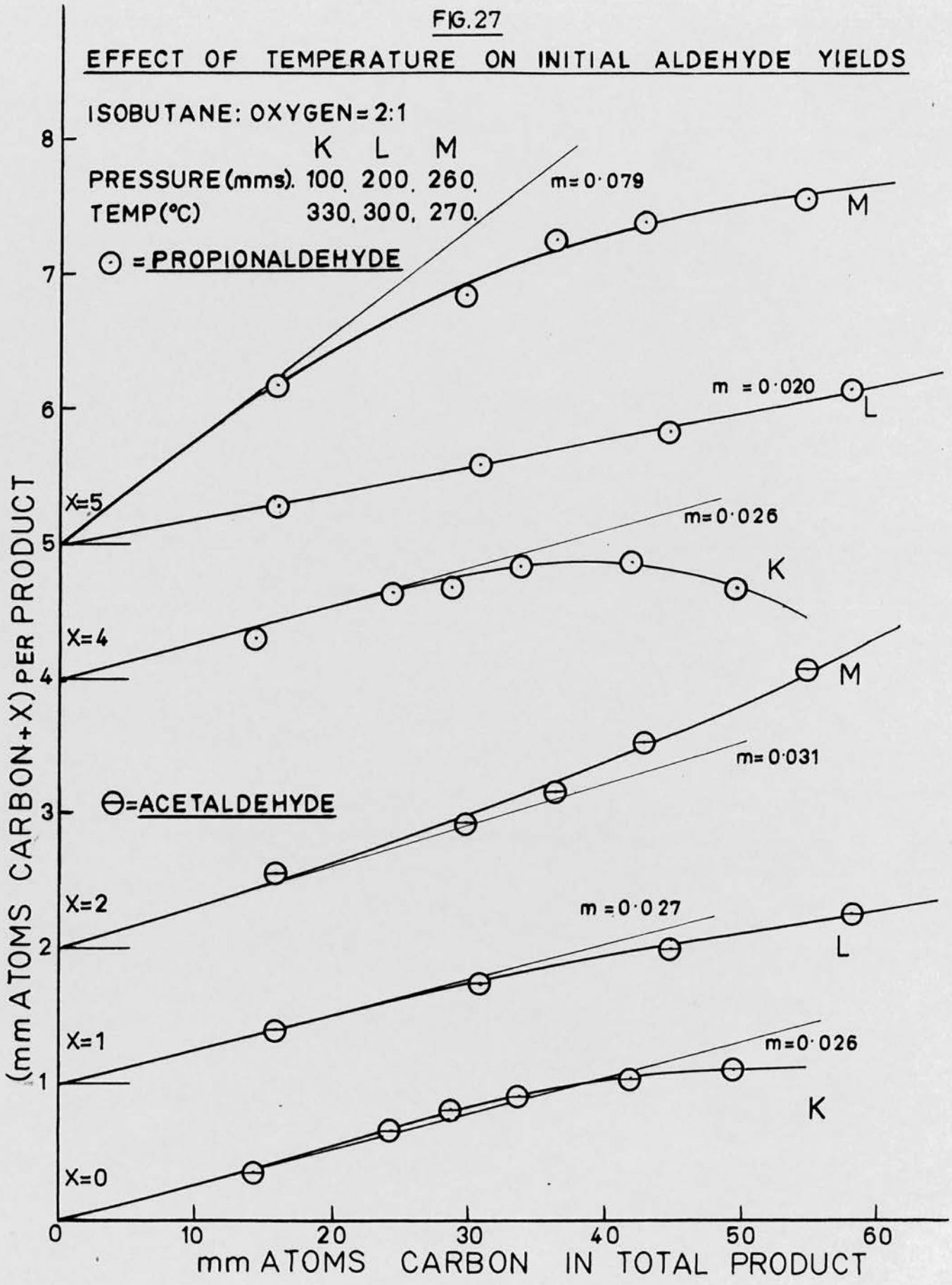


FIG. 28A.

PRODUCT DEVELOPMENT DURING ISOBUTANE OXIDATION AT 300°C.

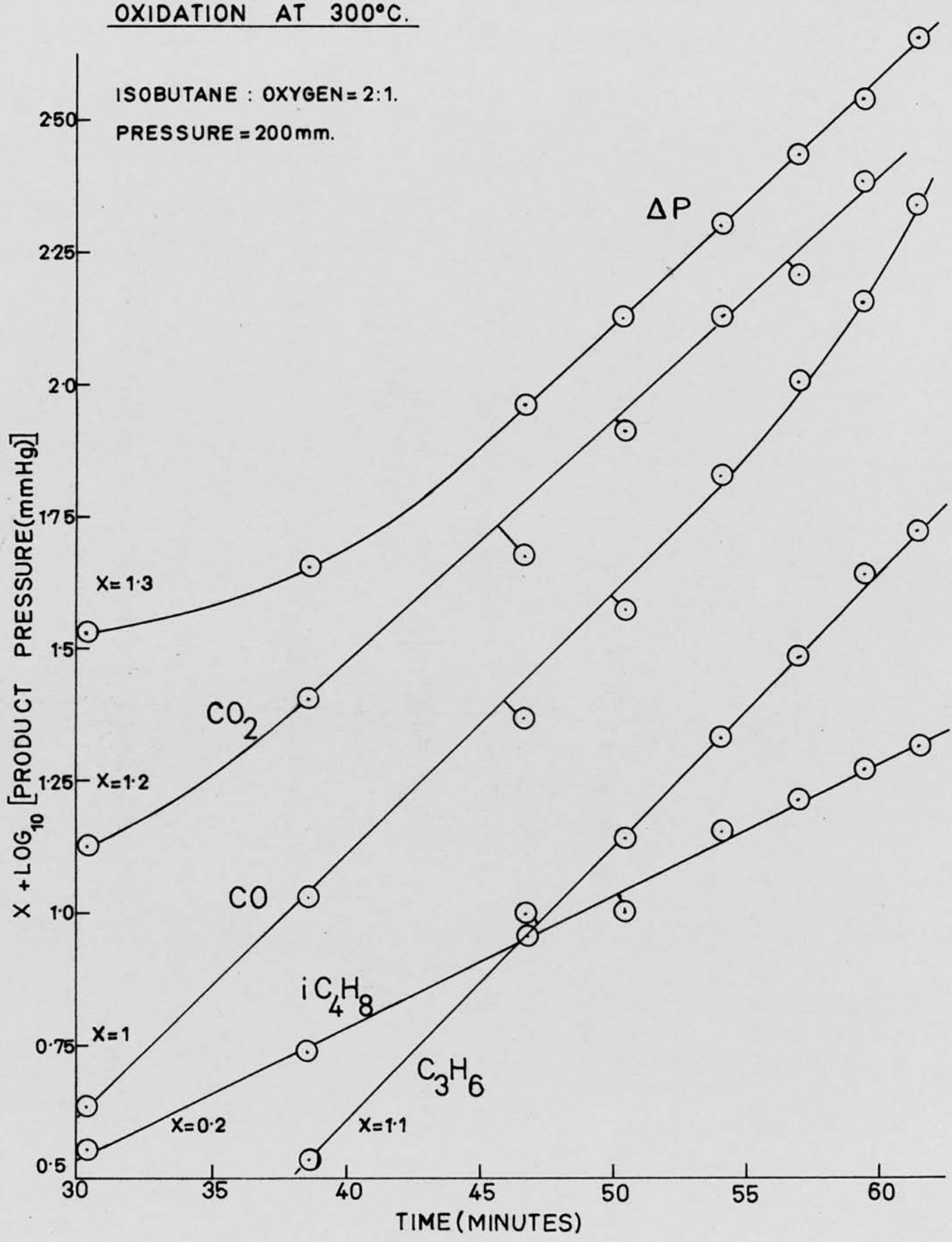
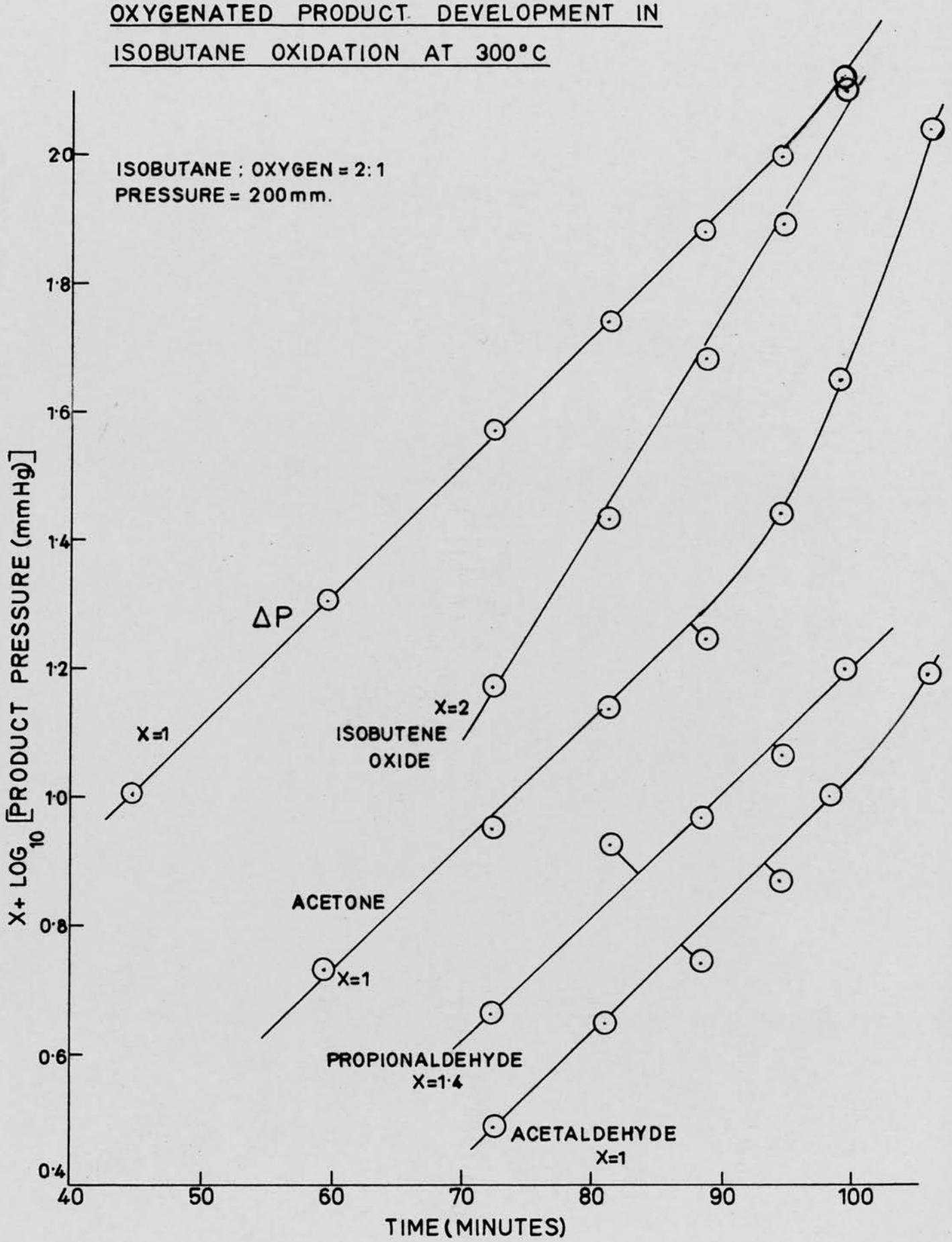
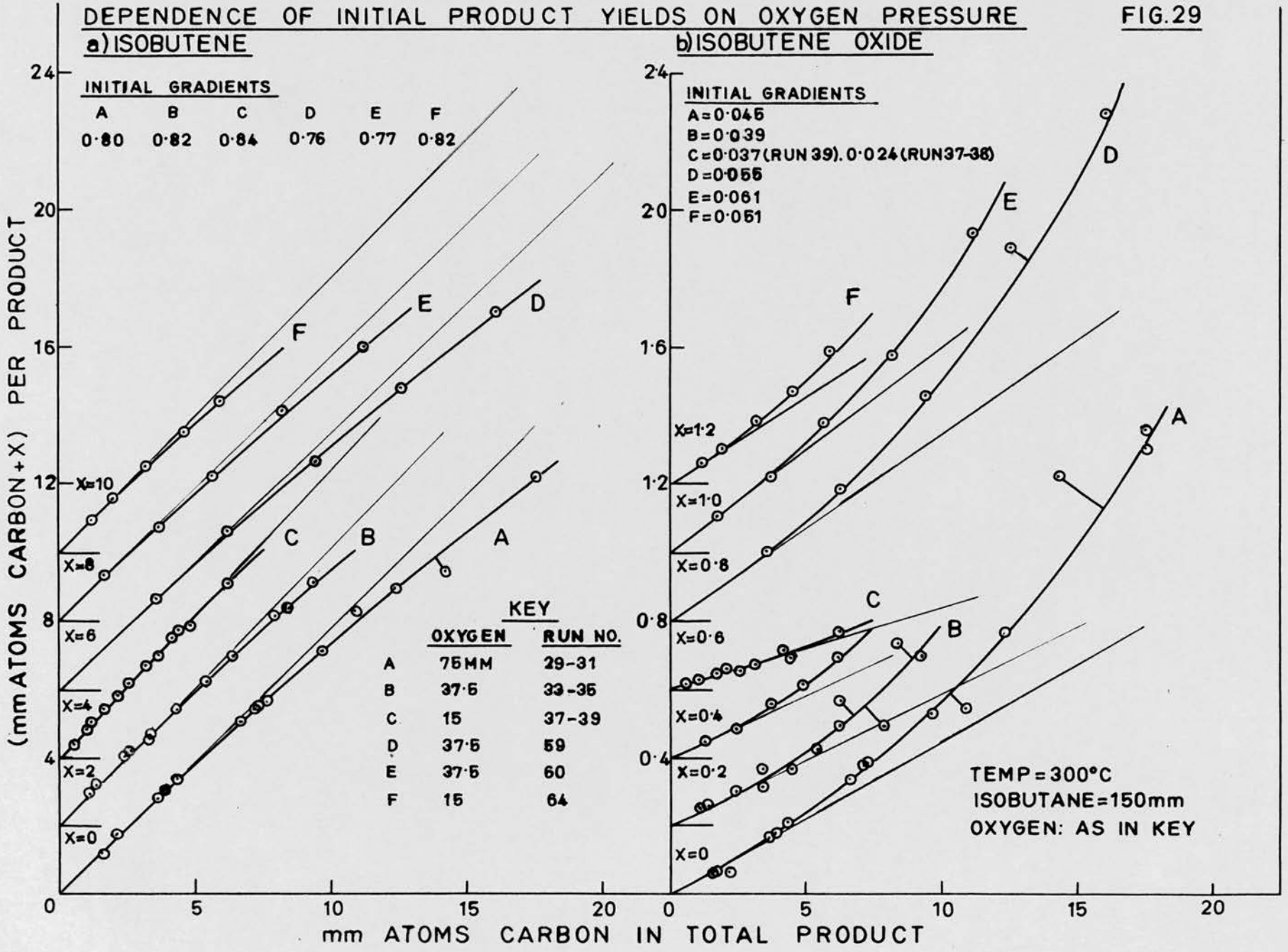
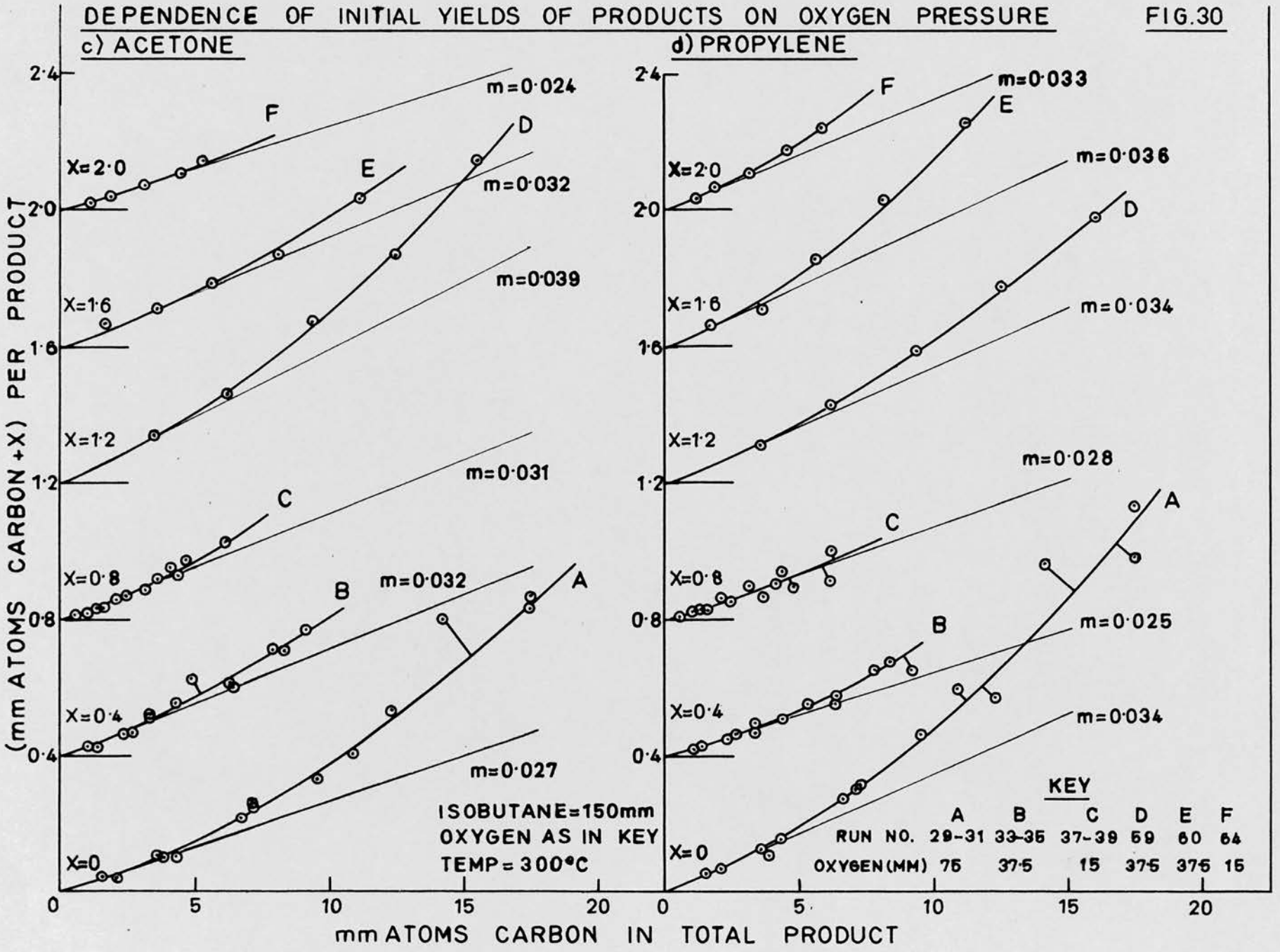


FIG. 28B.

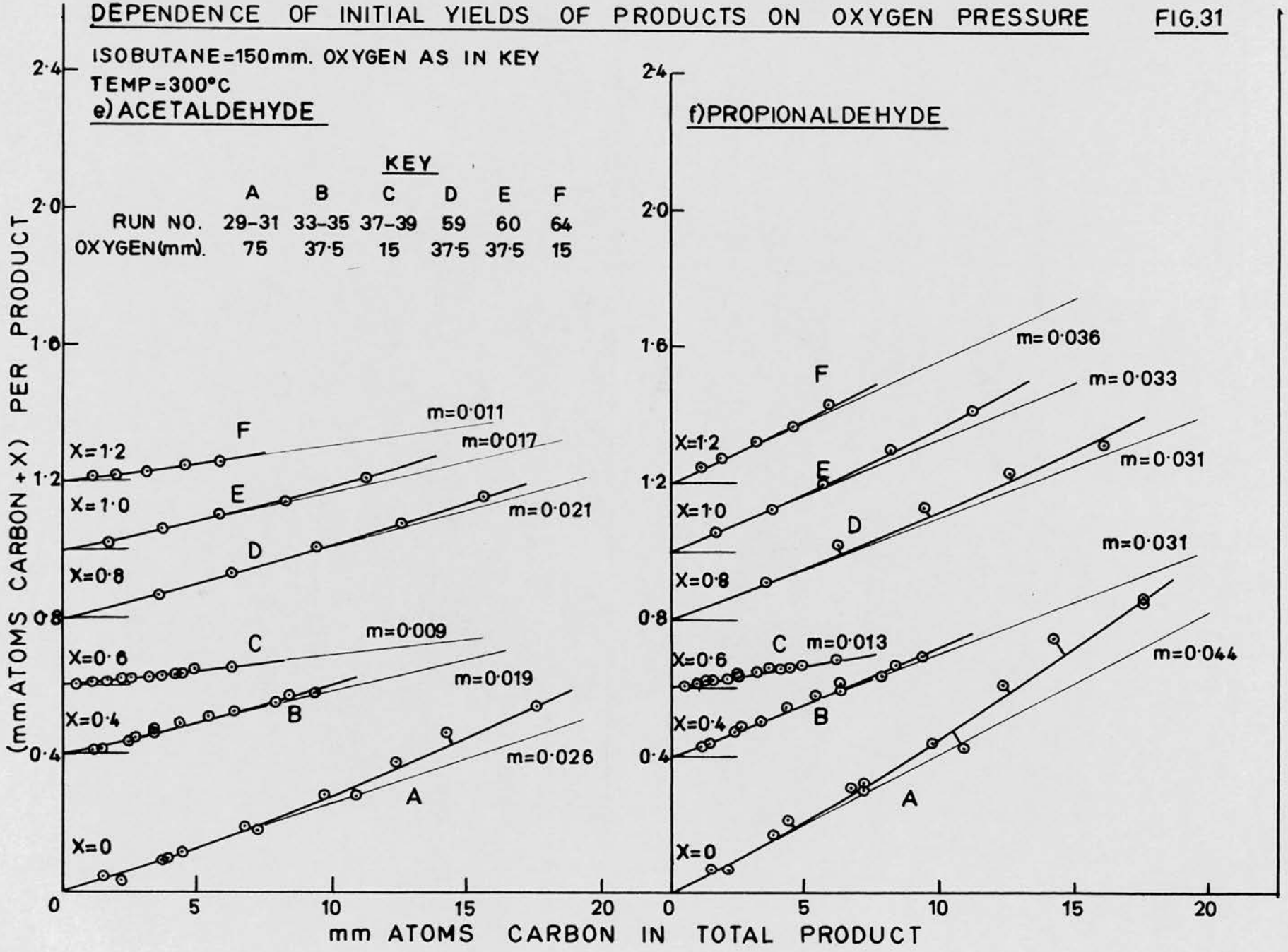
OXYGENATED PRODUCT DEVELOPMENT IN ISOBUTANE OXIDATION AT 300°C



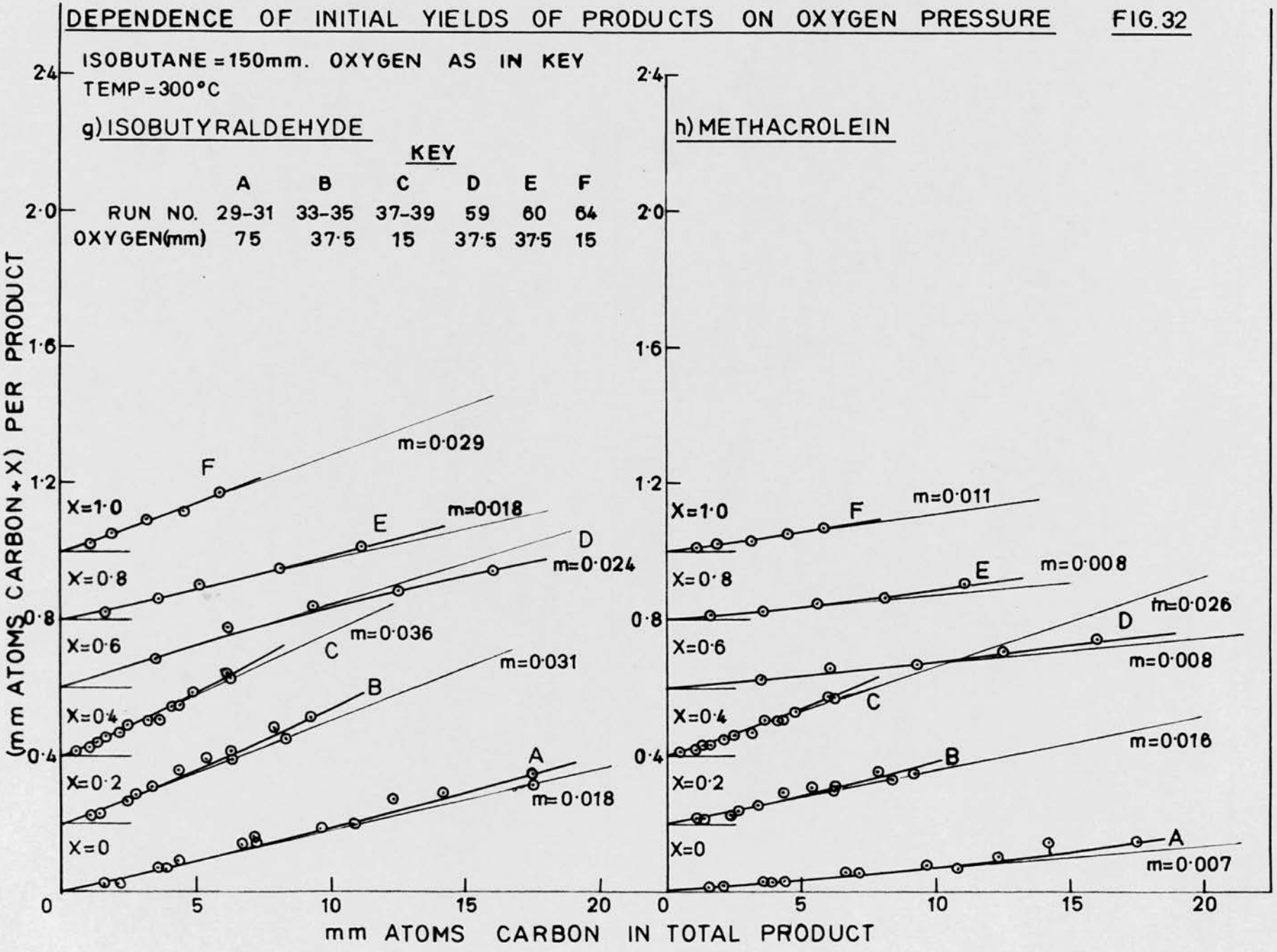

DEPENDENCE OF INITIAL PRODUCT YIELDS ON OXYGEN PRESSURE
FIG.29
a) ISOBUTENE
b) ISOBUTENE OXIDE
INITIAL GRADIENTS
A B C D E F
0·80 0·82 0·84 0·76 0·77 0·82
INITIAL GRADIENTS
A=0·045
B=0·039
C=0·037 (RUN 39). 0·024 (RUN 37-38)
D=0·055
E=0·061
F=0·051
(mm ATOMS CARBON + X) PER PRODUCT
mm ATOMS CARBON IN TOTAL PRODUCT
X=10
X=8
X=6
X=4
X=2
X=0
X=1·2
X=1·0
X=0·8
X=0·6
X=0·4
X=0·2
X=0
KEY
OXYGEN RUN NO.
A 75MM 29-31
B 37·5 33-35
C 15 37-39
D 37·5 59
E 37·5 60
F 15 64
TEMP = 300°C
ISOBUTANE = 150mm
OXYGEN: AS IN KEY

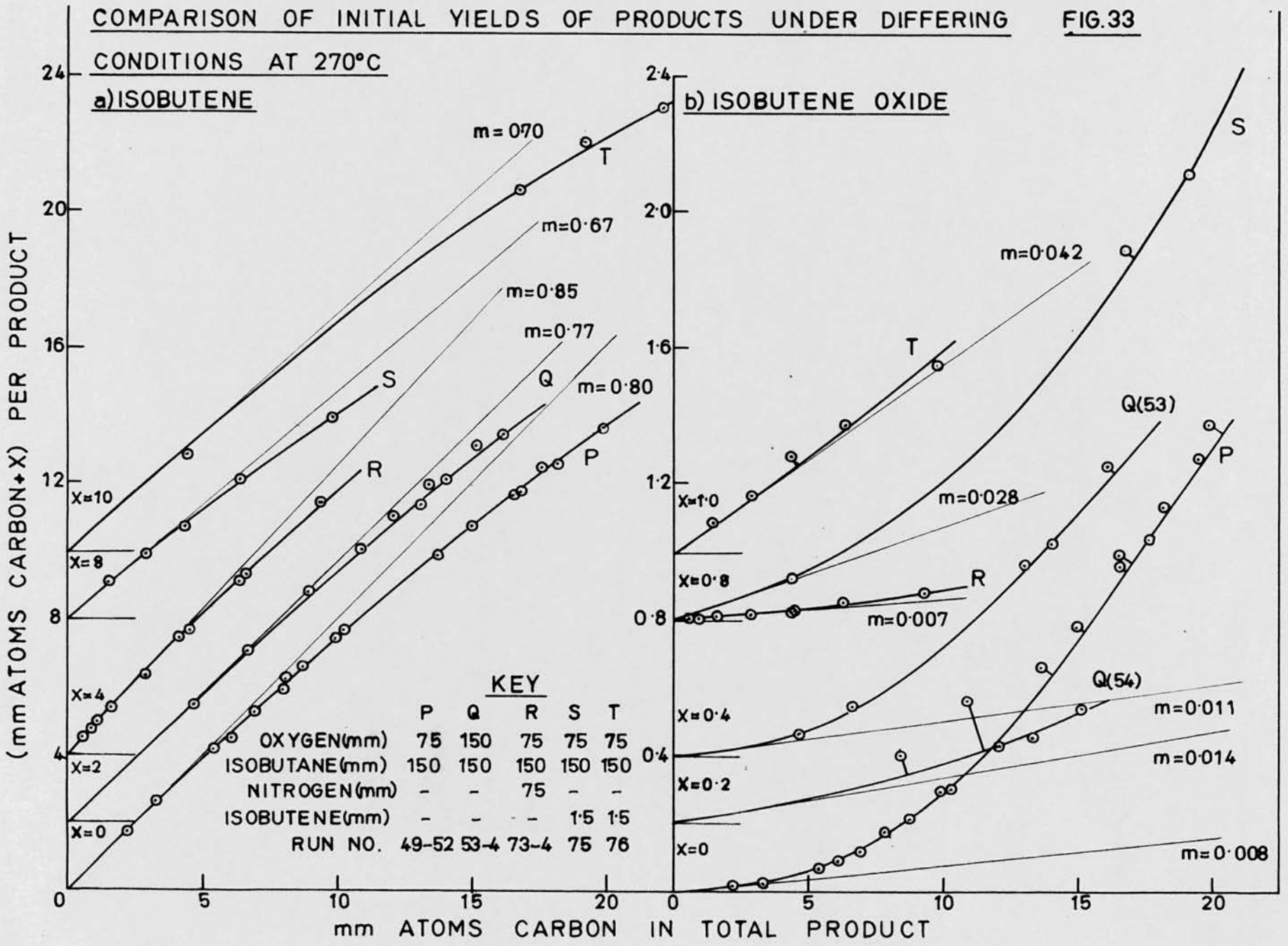

DEPENDENCE OF INITIAL YIELDS OF PRODUCTS ON OXYGEN PRESSURE
FIG.30
c) ACETONE
d) PROPYLENE
(mm ATOMS CARBON +X) PER PRODUCT
mm ATOMS CARBON IN TOTAL PRODUCT
X=2·0
X=1·6
X=1·2
X=0·8
X=0·4
X=0
m=0·024
m=0·032
m=0·039
m=0·031
m=0·032
m=0·027
m=0·033
m=0·036
m=0·034
m=0·028
m=0·025
m=0·034
ISOBUTANE=150mm
OXYGEN AS IN KEY
TEMP=300°C
KEY
A B C D E F
RUN NO. 29-31 33-35 37-39 59 60 64
OXYGEN(MM) 75 37·5 15 37·5 37·5 15

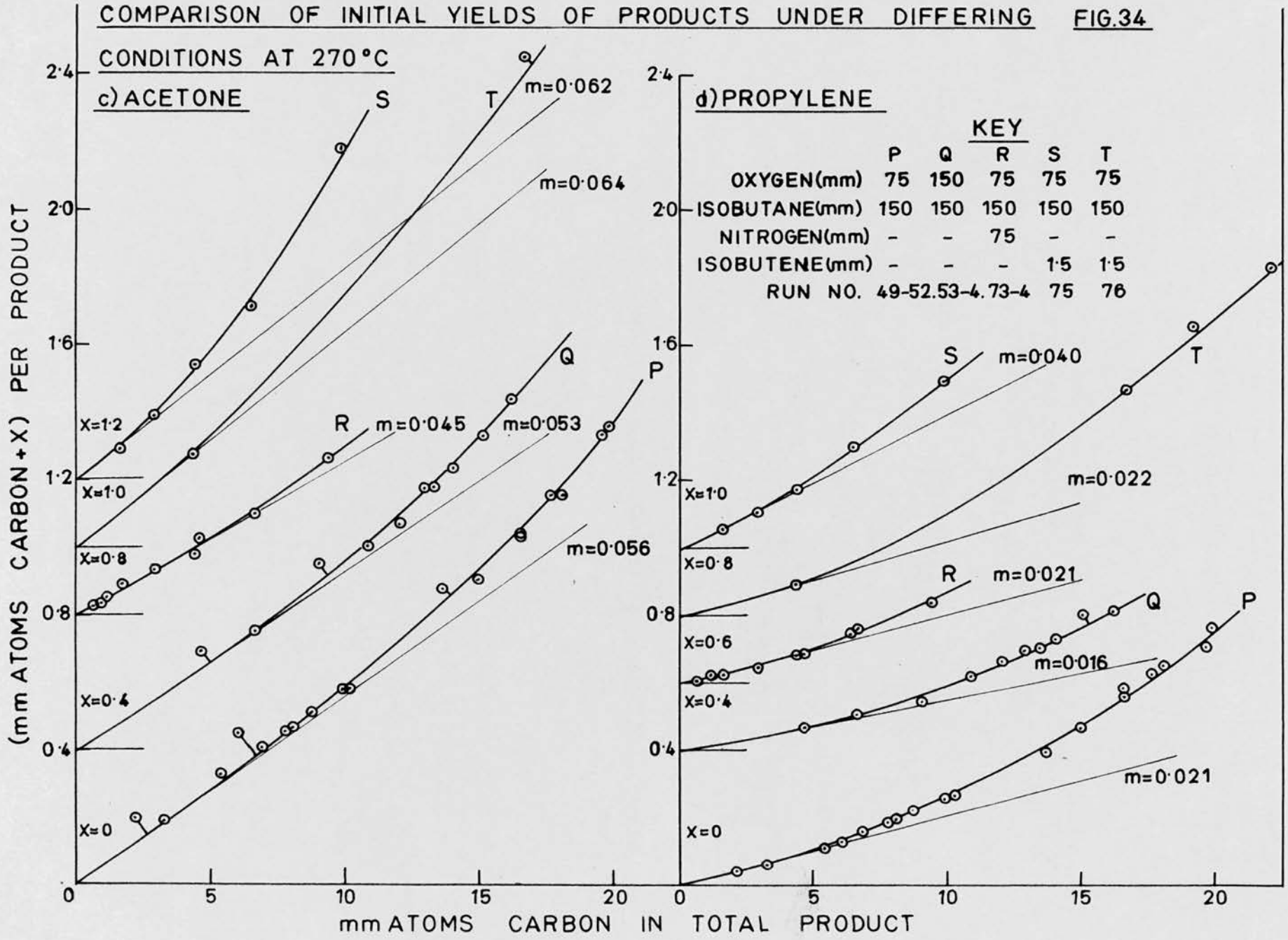
DEPENDENCE OF INITIAL YIELDS OF PRODUCTS ON OXYGEN PRESSURE FIG.31



DEPENDENCE OF INITIAL YIELDS OF PRODUCTS ON OXYGEN PRESSURE FIG. 32




COMPARISON OF INITIAL YIELDS OF PRODUCTS UNDER DIFFERING CONDITIONS AT 270°C
FIG.33
a) ISOBUTENE
b) ISOBUTENE OXIDE
(mm ATOMS CARBON + X) PER PRODUCT
mm ATOMS CARBON IN TOTAL PRODUCT
m = 0·70
m = 0·67
m = 0·85
m = 0·77
m = 0·80
X = 10
X = 8
X = 4
X = 2
X = 0
S
T
Q
R
P
m = 0·042
m = 0·028
m = 0·007
m = 0·011
m = 0·014
m = 0·008
X = 1·0
X = 0·8
X = 0·4
X = 0·2
X = 0
Q(53)
Q(54)
KEY
P Q R S T
OXYGEN (mm) 75 150 75 75 75
ISOBUTANE (mm) 150 150 150 150 150
NITROGEN (mm) – – 75 – –
ISOBUTENE (mm) – – – 1·5 1·5
RUN NO. 49–52 53–4 73–4 75 76


COMPARISON OF INITIAL YIELDS OF PRODUCTS UNDER DIFFERING CONDITIONS AT 270 °C
FIG.34
c) ACETONE
d) PROPYLENE
KEY
P Q R S T
OXYGEN(mm) 75 150 75 75 75
ISOBUTANE(mm) 150 150 150 150 150
NITROGEN(mm) - - 75 - -
ISOBUTENE(mm) - - - 1·5 1·5
RUN NO. 49-52.53-4.73-4 75 76
(mm ATOMS CARBON + X) PER PRODUCT
mm ATOMS CARBON IN TOTAL PRODUCT
m=0·062
m=0·064
m=0·045
m=0·053
m=0·056
m=0·040
m=0·022
m=0·021
m=0·016
m=0·021
X=1·2
X=1·0
X=0·8
X=0·4
X=0
X=0·6
S
T
Q
R
P

COMPARISON OF INITIAL YIELDS OF PRODUCTS UNDER DIFFERING CONDITIONS AT 270°C

FIG.35

e) ACETALDEHYDE

f) PROPIONALDEHYDE

KEY

	P	Q	R	S	T
OXYGEN (mm)	75	150	75	75	75
ISOBUTANE (mm)	150	150	150	150	150
NITROGEN (mm)	-	-	75	-	-
ISOBUTENE (mm)	-	-	-	1·5	1·5
RUN NO.	49-52	52-3	73-4	75	76

(mm ATOMS CARBON+X) PER PRODUCT

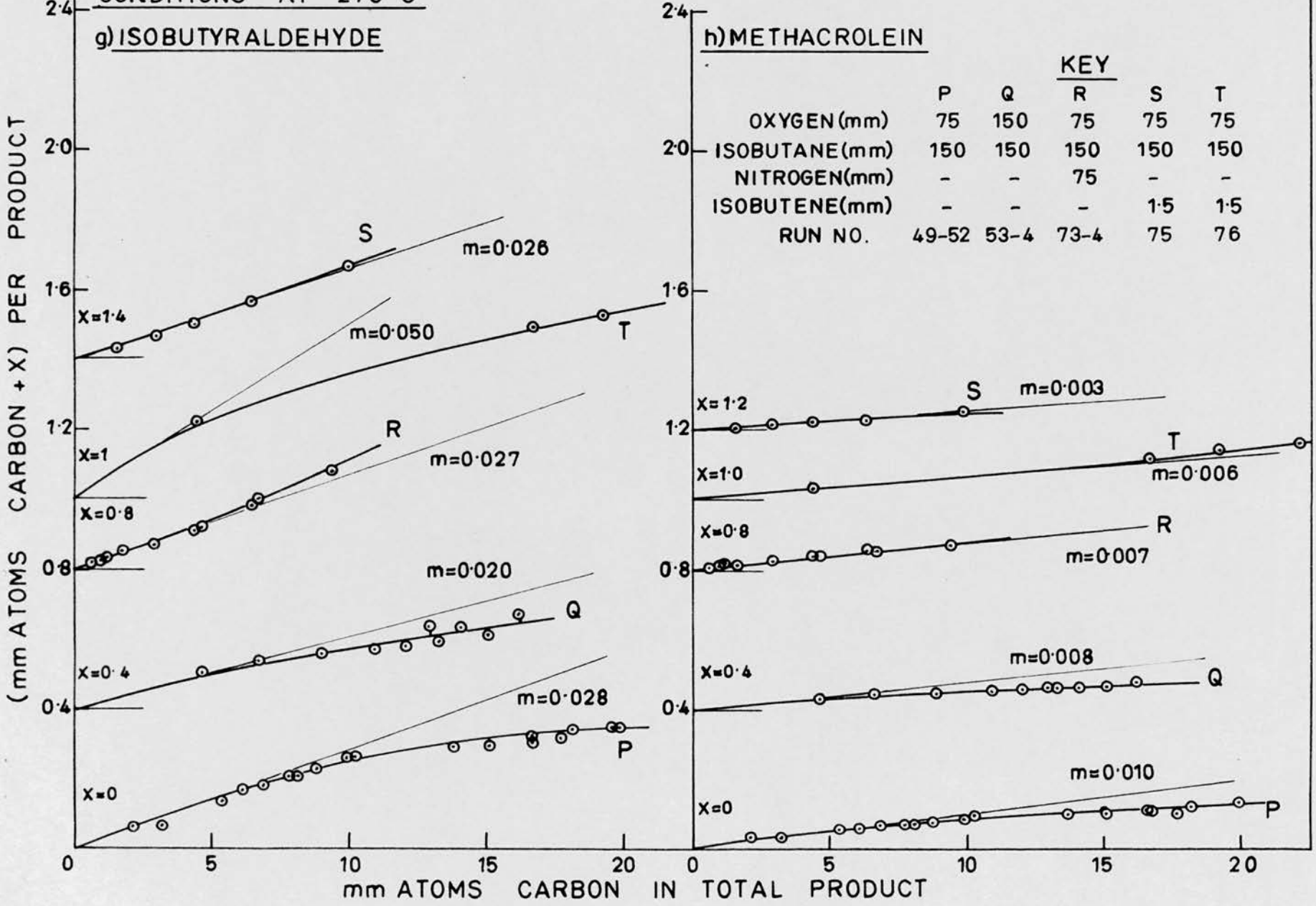
mm ATOMS CARBON IN TOTAL PRODUCT

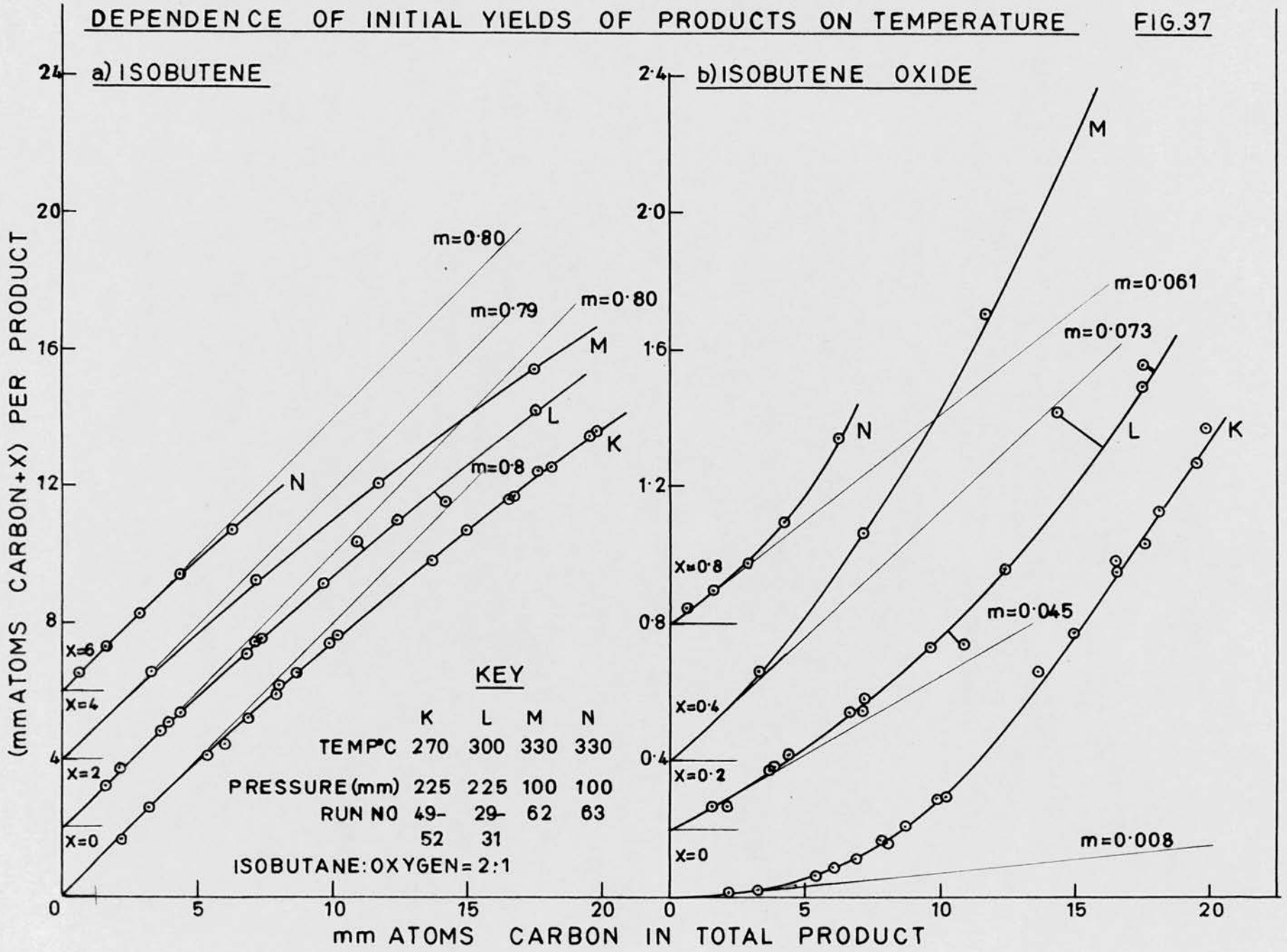
m=0·022 S T X=1·0 X=0·6 m=0·016 X=0·6 R m=0·014 Q m=0·020 X=0·2 P m=0·018 X=0

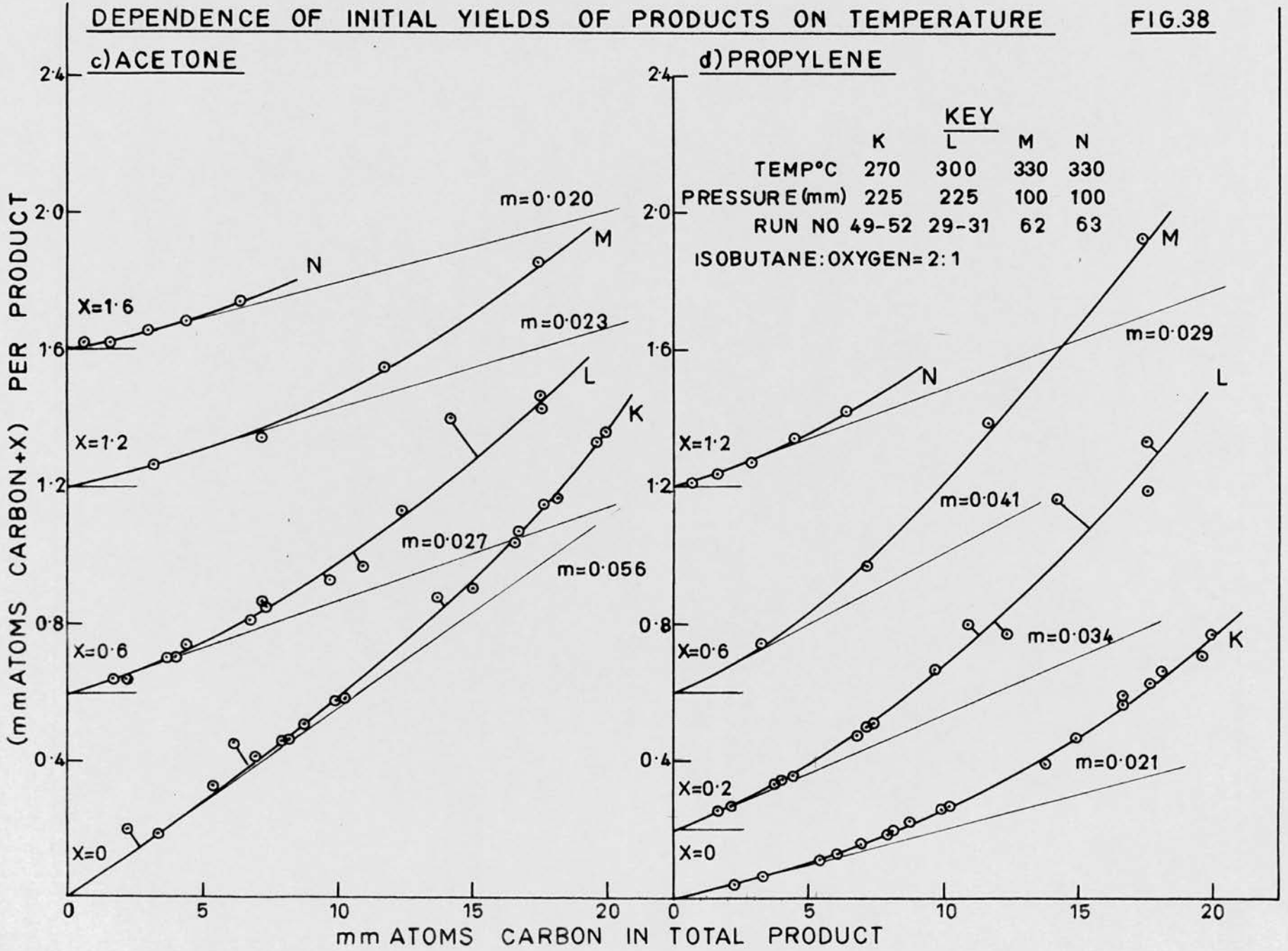
m=0·087 S T m=0·061 X=1 X=0·6 m=0·047 R Q m=0·053 X=0·6 P m=0·034 X=0·2 X=0

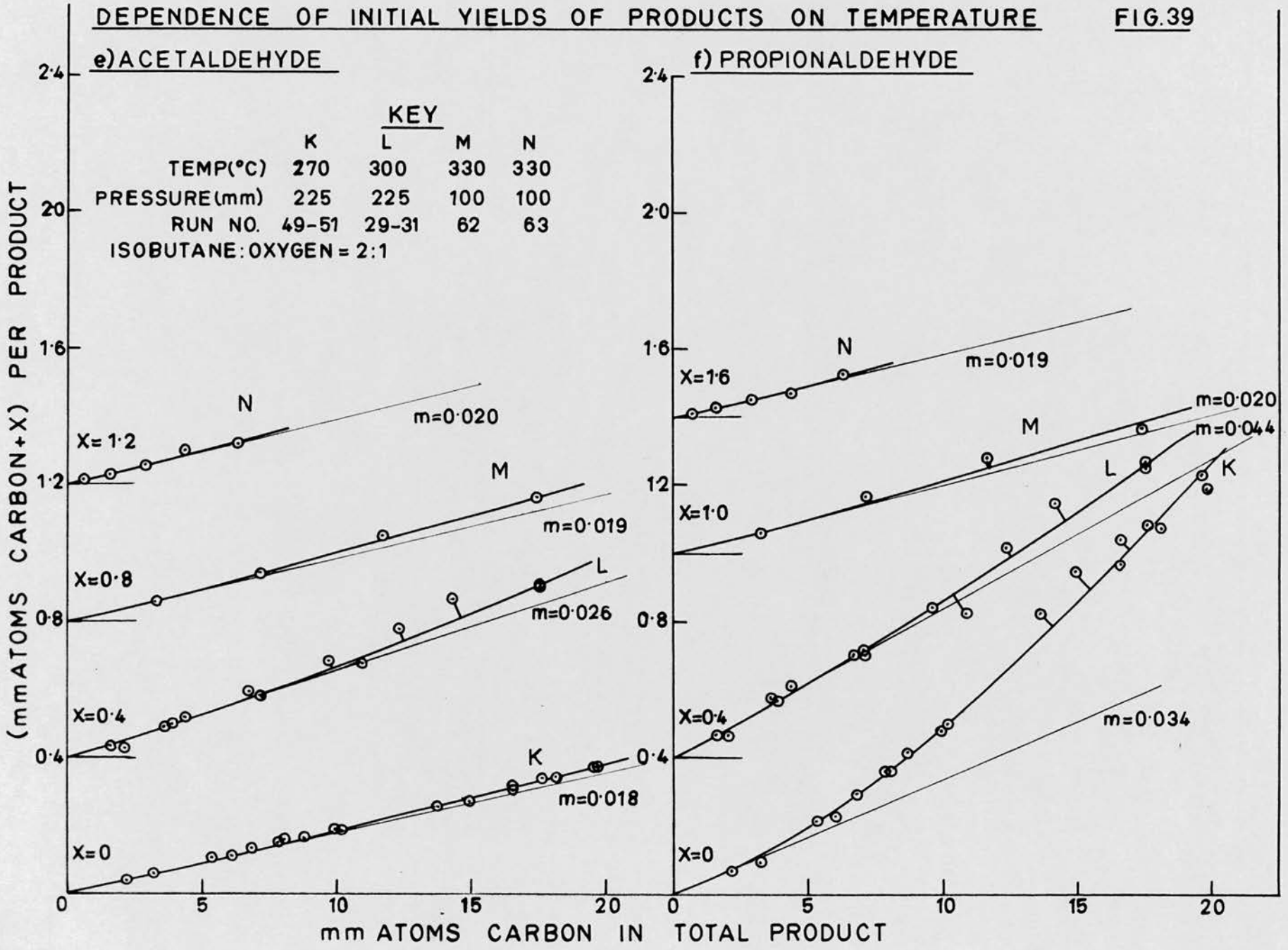
COMPARISON OF INITIAL YIELDS OF PRODUCTS UNDER DIFFERING CONDITIONS AT 270°C

FIG.36




DEPENDENCE OF INITIAL YIELDS OF PRODUCTS ON TEMPERATURE
FIG.37
a) ISOBUTENE
b) ISOBUTENE OXIDE
(mm ATOMS CARBON+X) PER PRODUCT
mm ATOMS CARBON IN TOTAL PRODUCT
m=0·80
m=0·79
m=0·80
m=0·8
m=0·061
m=0·073
m=0·045
m=0·008
X=6
X=4
X=2
X=0
X=0·8
X=0·4
X=0·2
X=0
K
L
M
N
KEY
K L M N
TEMP°C 270 300 330 330
PRESSURE(mm) 225 225 100 100
RUN NO 49-52 29-31 62 63
ISOBUTANE:OXYGEN = 2:1


DEPENDENCE OF INITIAL YIELDS OF PRODUCTS ON TEMPERATURE
FIG.38
c) ACETONE
d) PROPYLENE
KEY
K L M N
TEMP°C 270 300 330 330
PRESSURE (mm) 225 225 100 100
RUN NO 49-52 29-31 62 63
ISOBUTANE: OXYGEN = 2:1
(mm ATOMS CARBON + X) PER PRODUCT
mm ATOMS CARBON IN TOTAL PRODUCT
m=0·020
m=0·023
m=0·027
m=0·056
m=0·029
m=0·041
m=0·034
m=0·021
X=1·6
X=1·2
X=0·6
X=0
X=1·2
X=0·6
X=0·2
X=0
K
L
M
N
0
5
10
15
20
0·4
0·8
1·2
1·6
2·0
2·4


DEPENDENCE OF INITIAL YIELDS OF PRODUCTS ON TEMPERATURE
FIG.39
e) ACETALDEHYDE
f) PROPIONALDEHYDE
KEY
K L M N
TEMP(°C) 270 300 330 330
PRESSURE(mm) 225 225 100 100
RUN NO. 49-51 29-31 62 63
ISOBUTANE: OXYGEN = 2:1
(mmATOMS CARBON+X) PER PRODUCT
mm ATOMS CARBON IN TOTAL PRODUCT
X=1·2
X=0·8
X=0·4
X=0
X=1·6
X=1·0
m=0·020
m=0·019
m=0·026
m=0·018
m=0·034
m=0·044
N
M
L
K
0
5
10
15
20
0·4
0·8
1·2
1·6
2·0
2·4

DEPENDENCE OF INITIAL YIELDS OF PRODUCTS ON TEMPERATURE

FIG.40

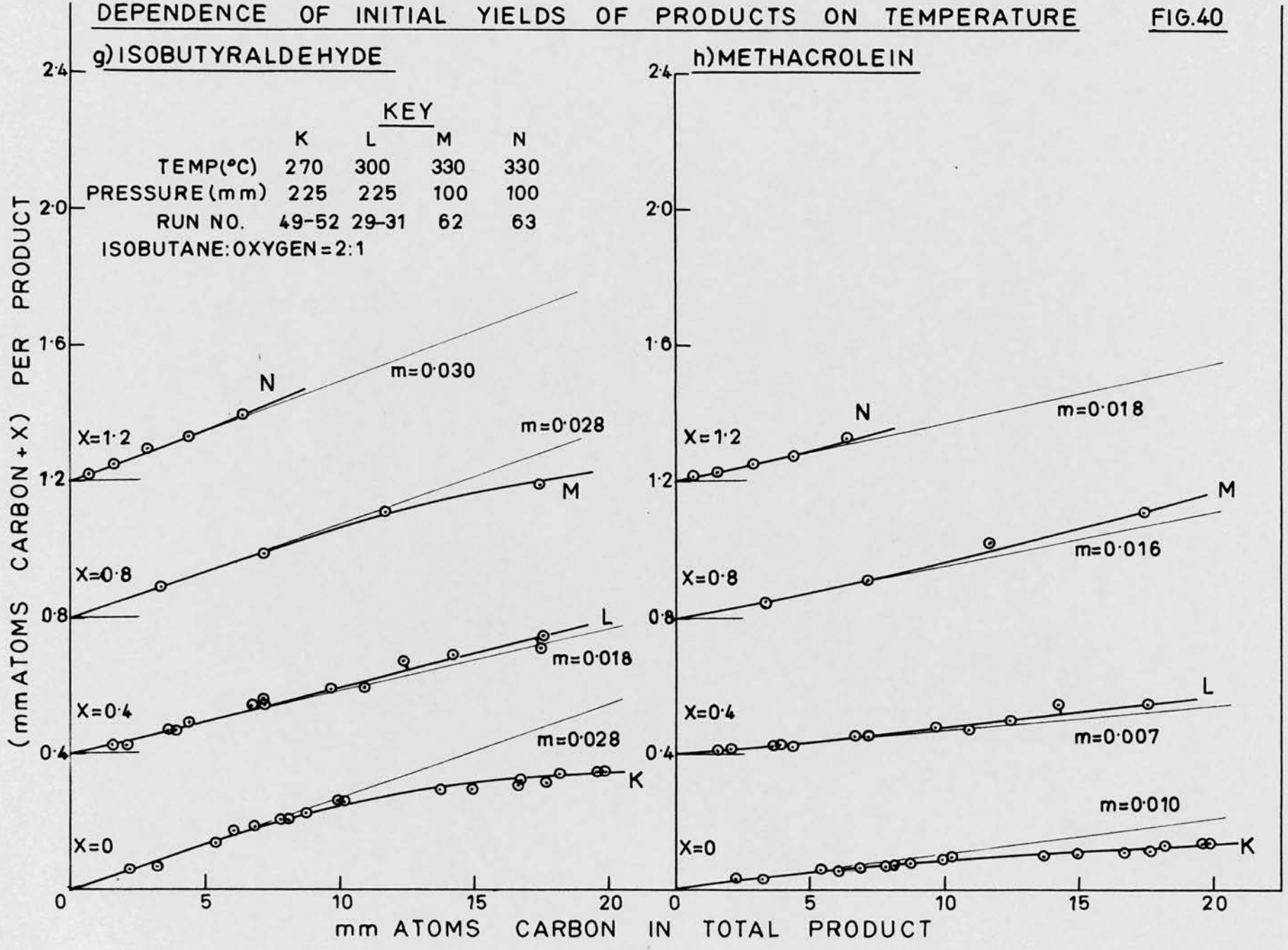


FIG.41

PRODUCT DEVELOPMENT DURING THE INDUCTION PERIOD

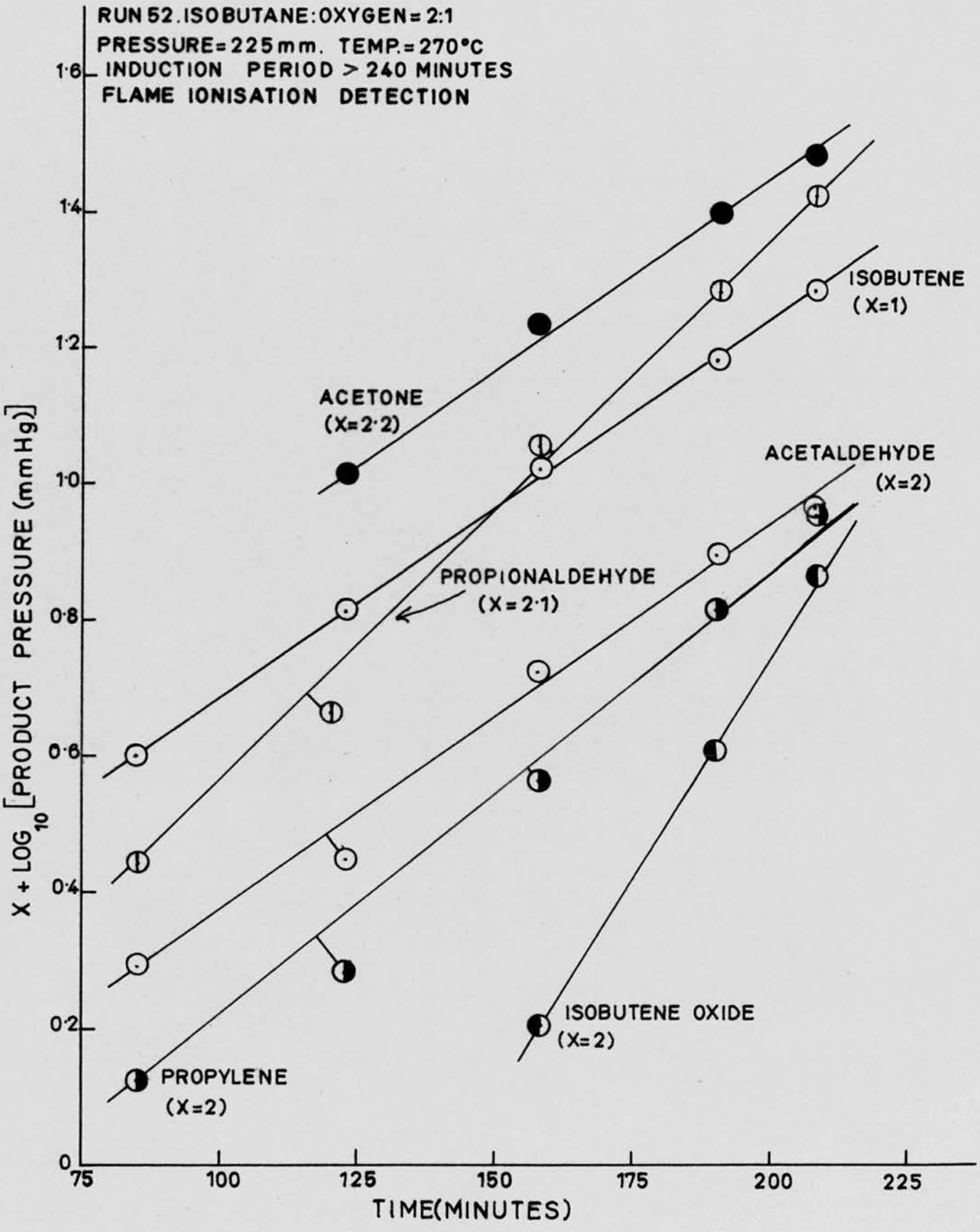
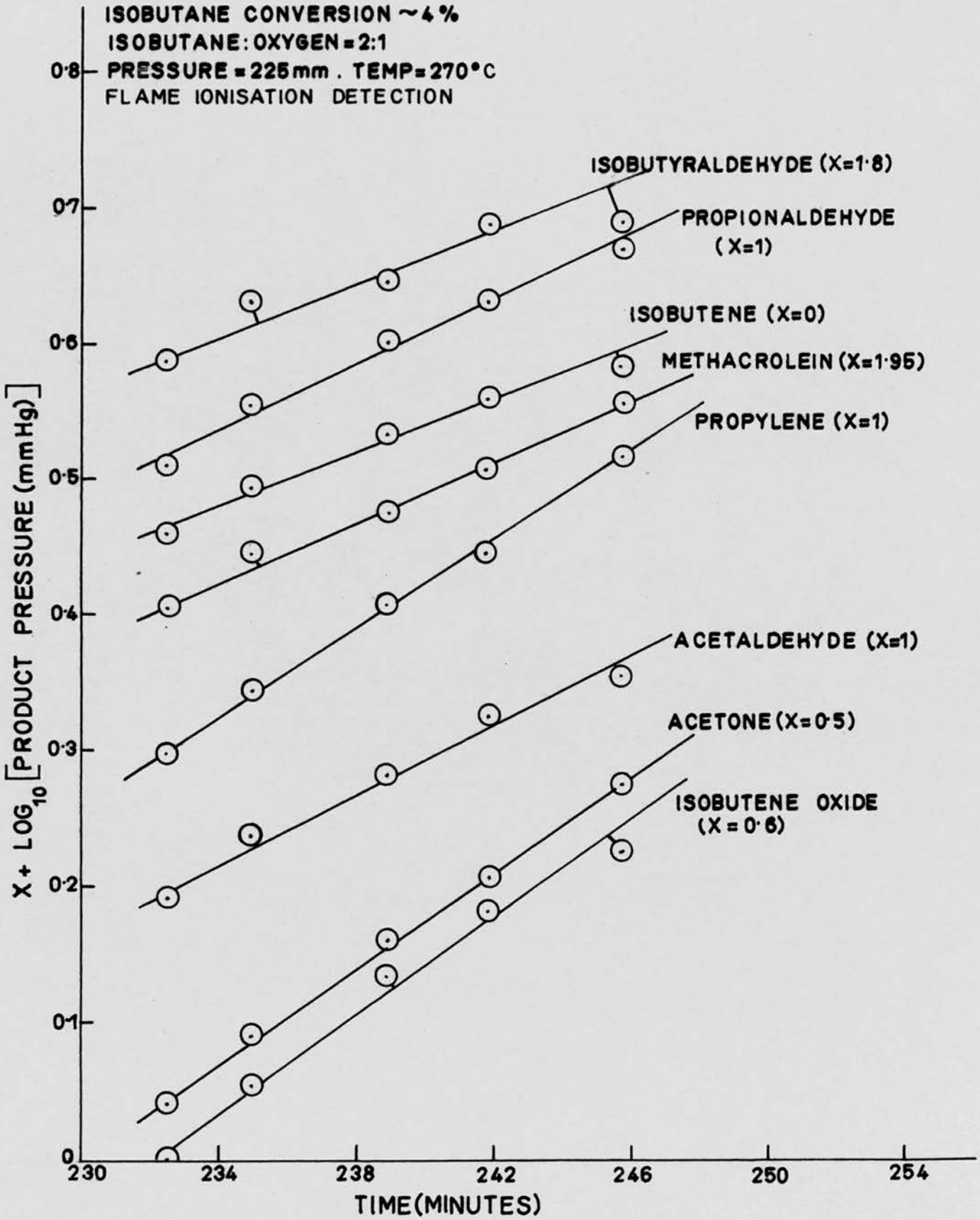


FIG.42

PRODUCT DEVELOPMENT IN THE EARLY STAGES OF ISOBUTANE OXIDATION.



VARIATION OF INITIAL YIELDS OF PRODUCTS IN SUCCESSIVE RUNS AT 330°C

ISOBUTANE:OXYGEN= 2:1. PRESSURE=100mm.

FIG. 43

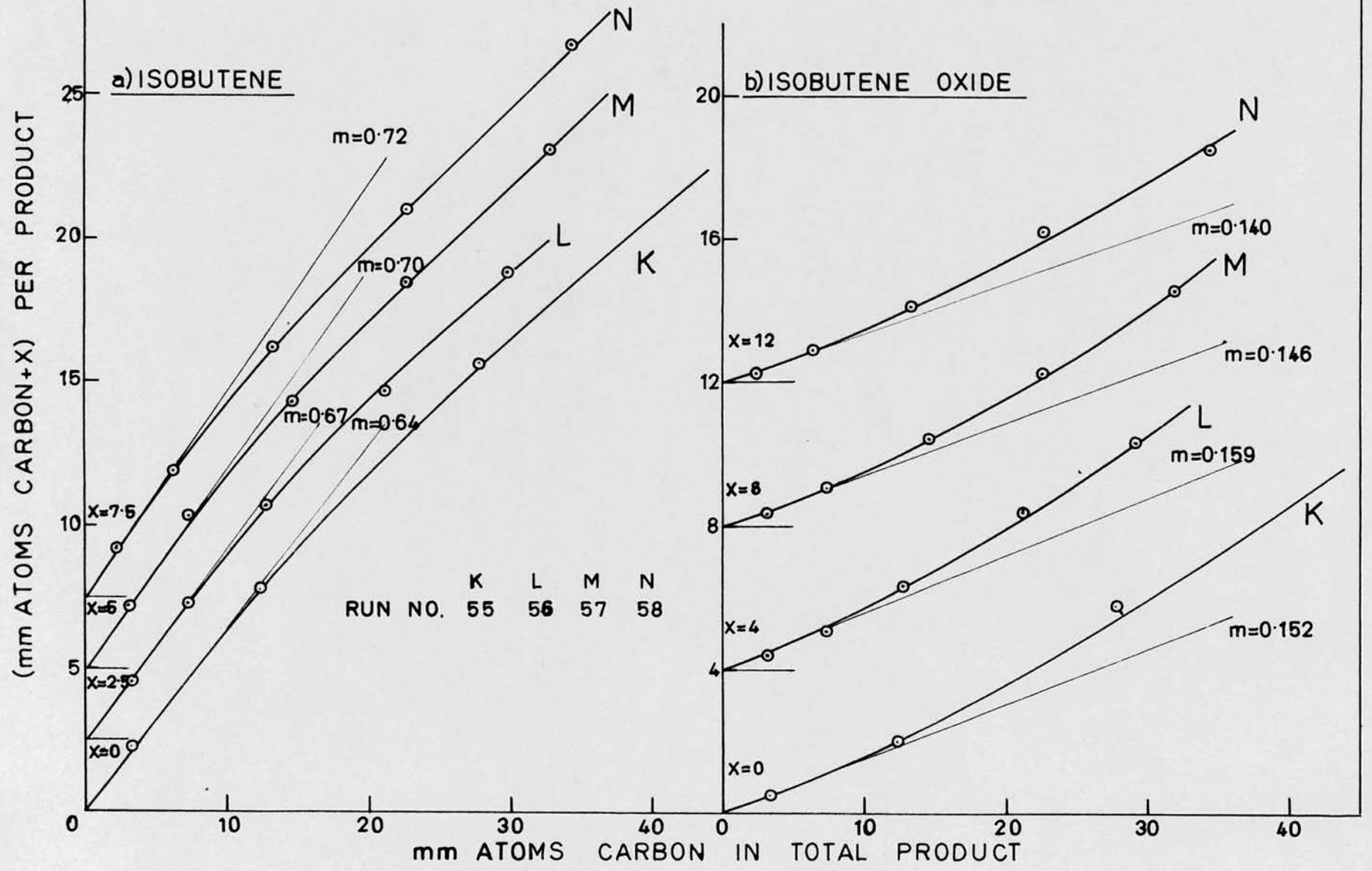


FIG. 44

VARIATION OF INITIAL YIELDS OF PRODUCTS IN SUCCESSIVE RUNS AT 330°C

ISOBUTANE : OXYGEN = 2:1. PRESSURE = 100 mm.

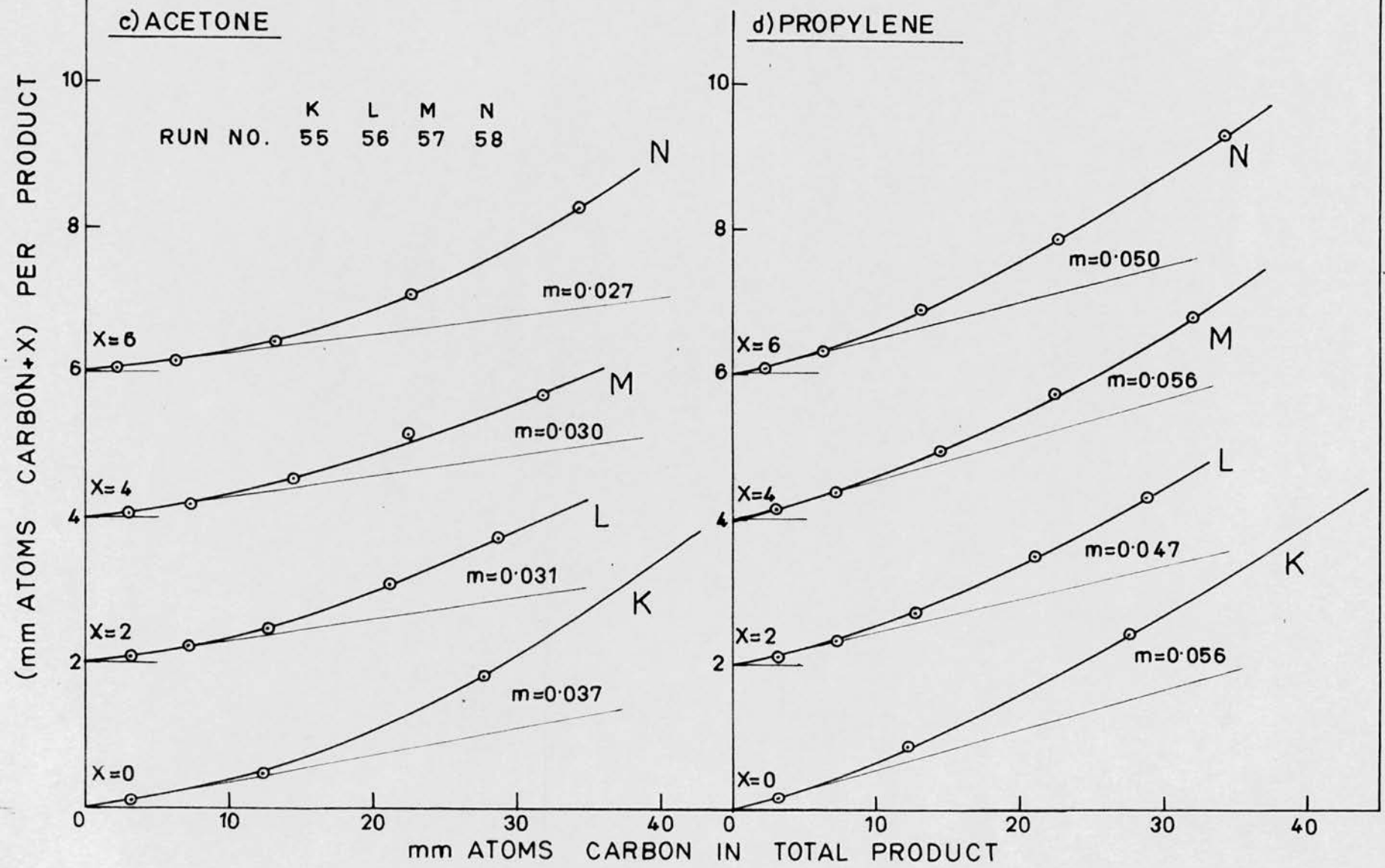


FIG.45

VARIATION OF INITIAL YIELDS OF PRODUCTS IN SUCCESSIVE RUNS AT 330°C

ISOBUTANE:OXYGEN= 2:1. PRESSURE=100mm.

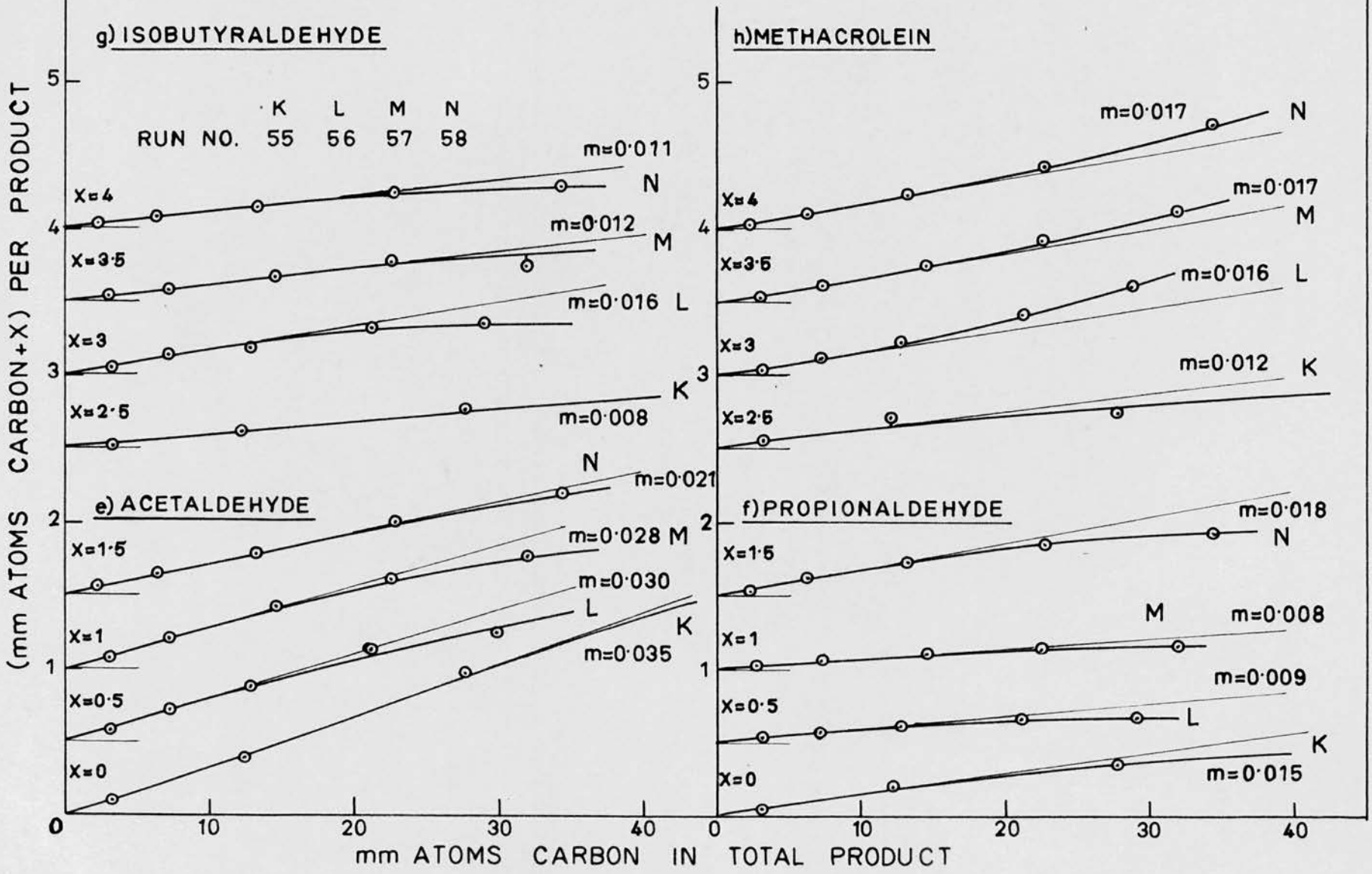


FIG. 46

GRAPH OF INITIAL PRODUCT YIELDS IN PROPANE OXIDATION AT 300°C

PROPANE = 150mm. OXYGEN = 75mm.

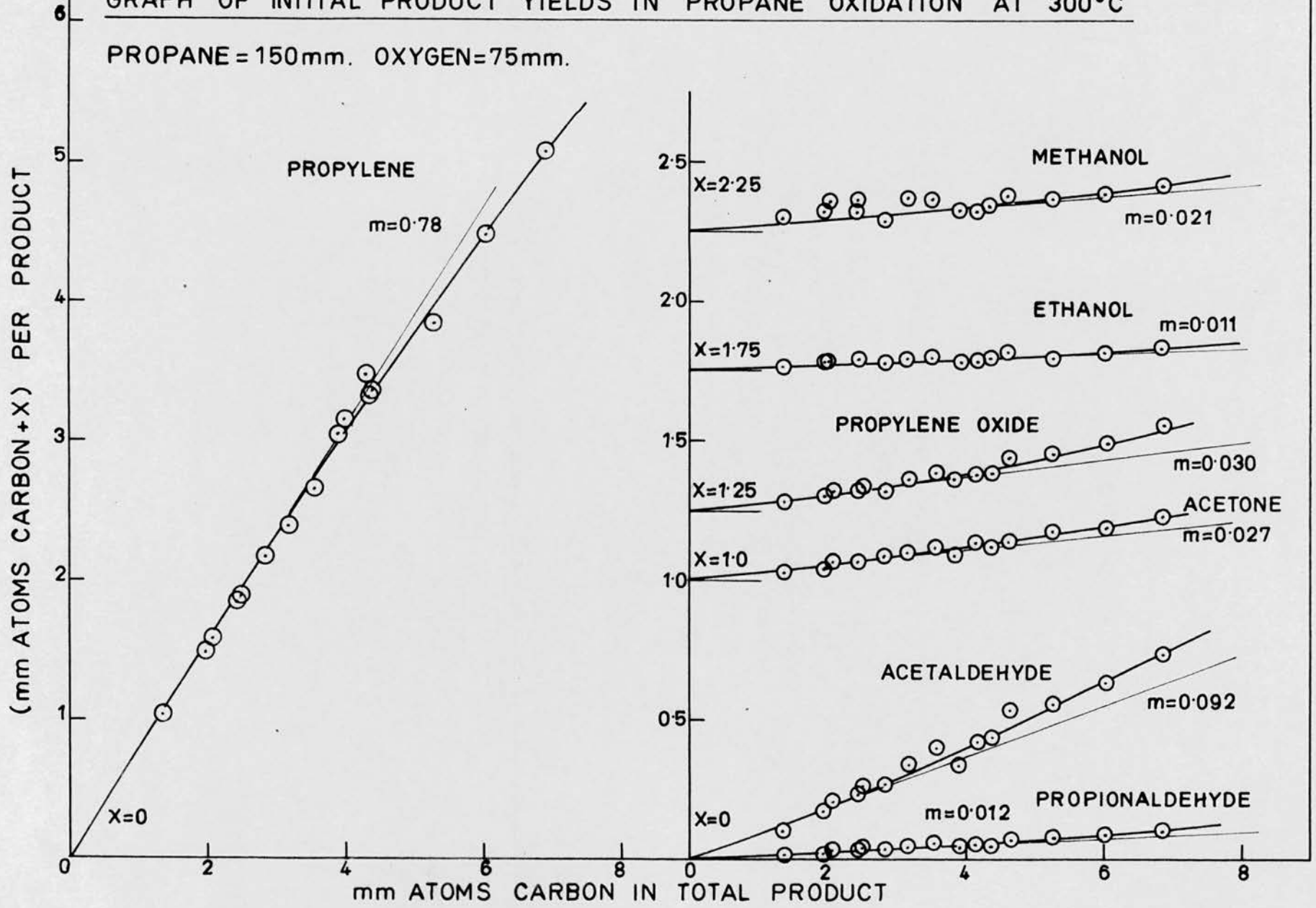


FIG. 47

VARIATION OF INITIAL YIELDS OF PRODUCTS WITH CHANGE IN REACTION VESSEL SURFACE

ISOBUTANE = 150mm
OXYGEN = 75mm
TEMP AS IN KEY

KEY

	R V SURFACE	TEMP(°C)	RUN NO
A	CLEAN PYREX	300	29-31
B	POTASSIUM CHLORIDE	300	67
C	ditto	300	68
D	CLEAN PYREX	270	49-52
E	BORIC ACID	270	65
F	ditto	270	66
G	HF WASHED	270	69

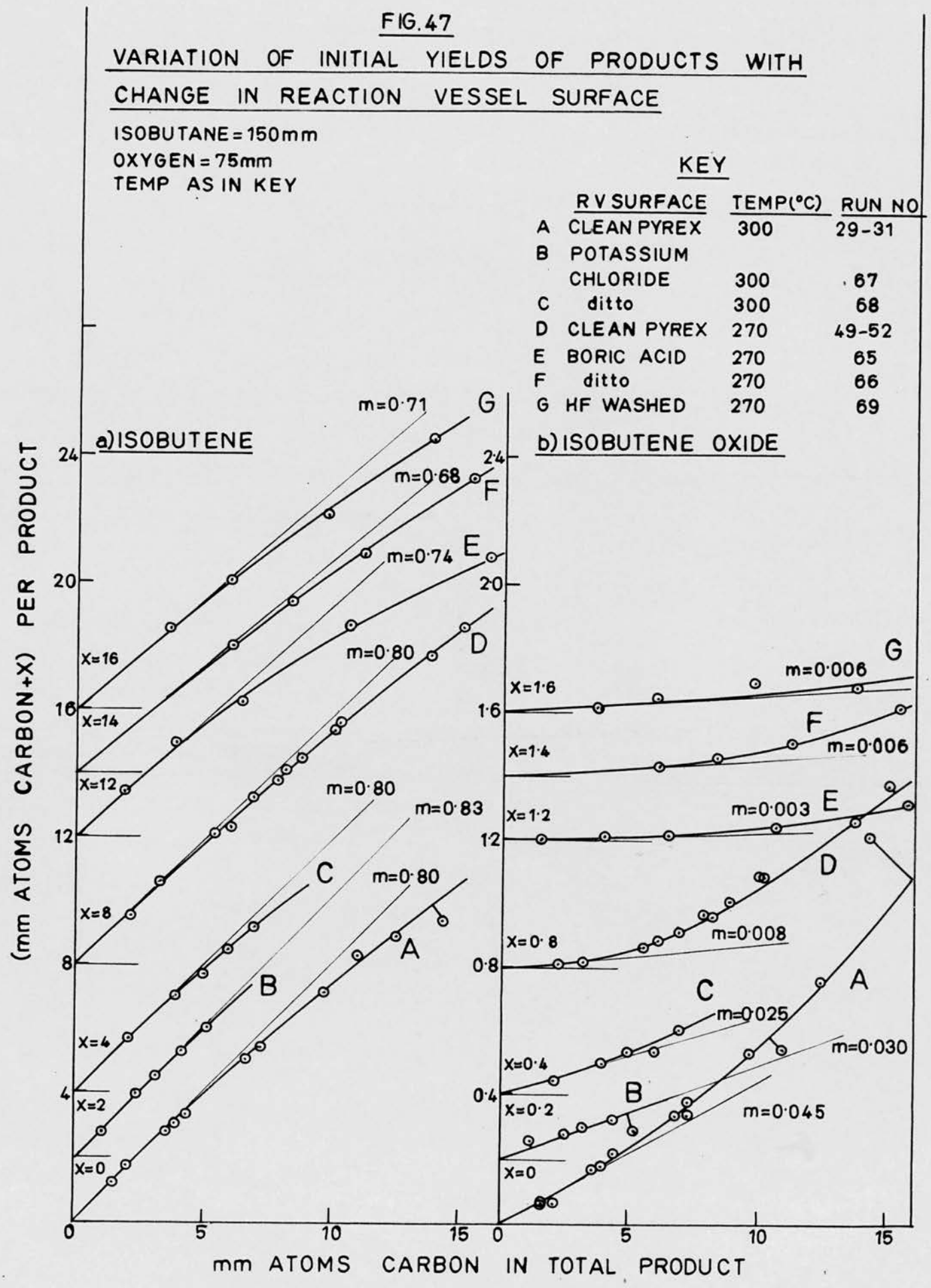


FIG. 48

VARIATION OF INITIAL YIELDS OF PRODUCTS WITH CHANGE IN REACTION VESSEL SURFACE

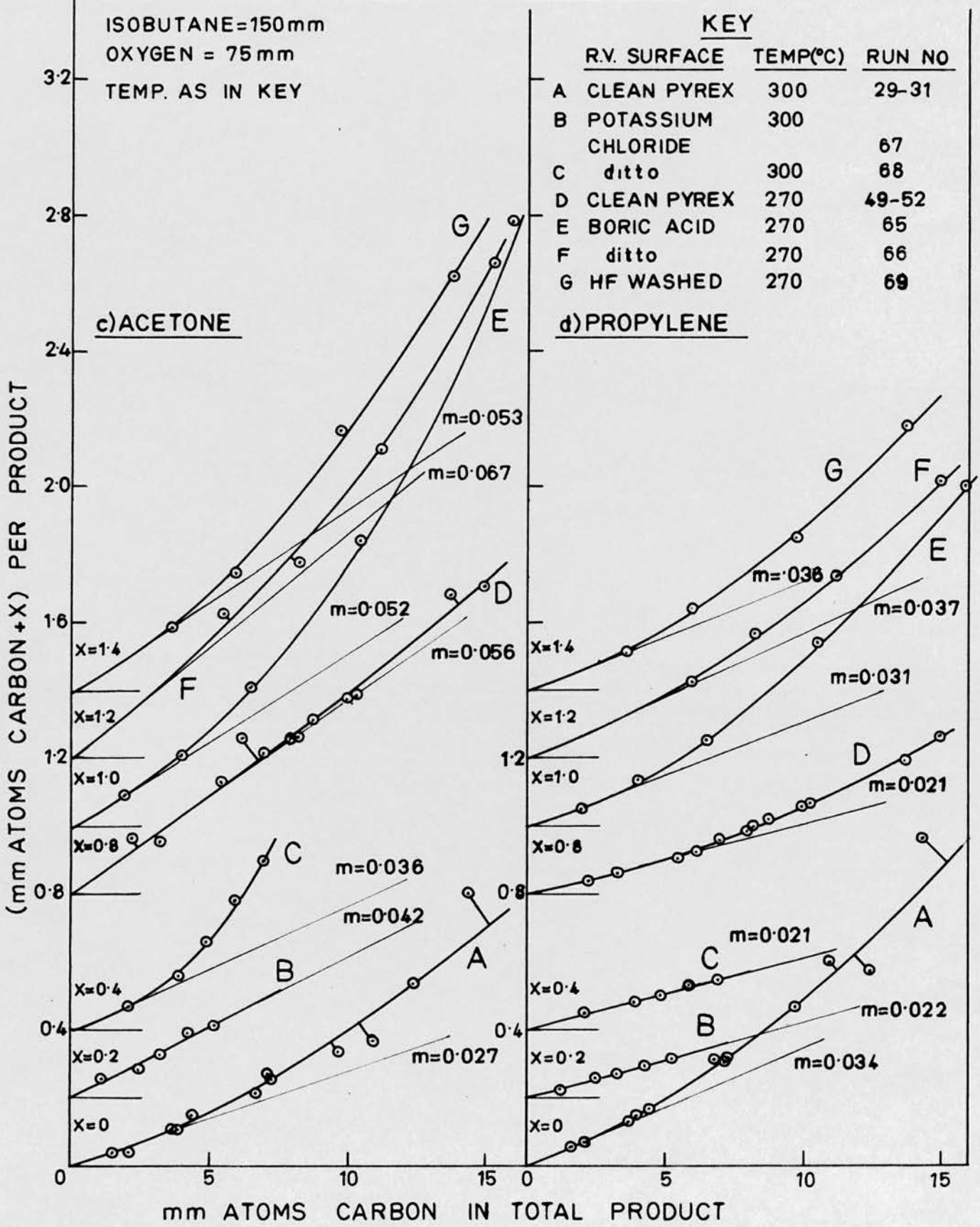


FIG.49

VARIATION OF INITIAL YIELDS OF PRODUCTS WITH CHANGE IN REACTION VESSEL SURFACE

ISOBUTANE = 150mm. OXYGEN = 75mm. TEMP. AS IN KEY

e) ACETALDEHYDE

f) PROPIONALDEHYDE

KEY

	R.V. SURFACE	TEMP(°C)	RUN NO.
A	CLEAN PYREX	300	29-31
B	POTASSIUM CHLORIDE	300	67
C	ditto	300	68
D	CLEAN PYREX	270	49-52
E	BORIC ACID	270	65
F	ditto	270	66
G	HF WASHED	270	69

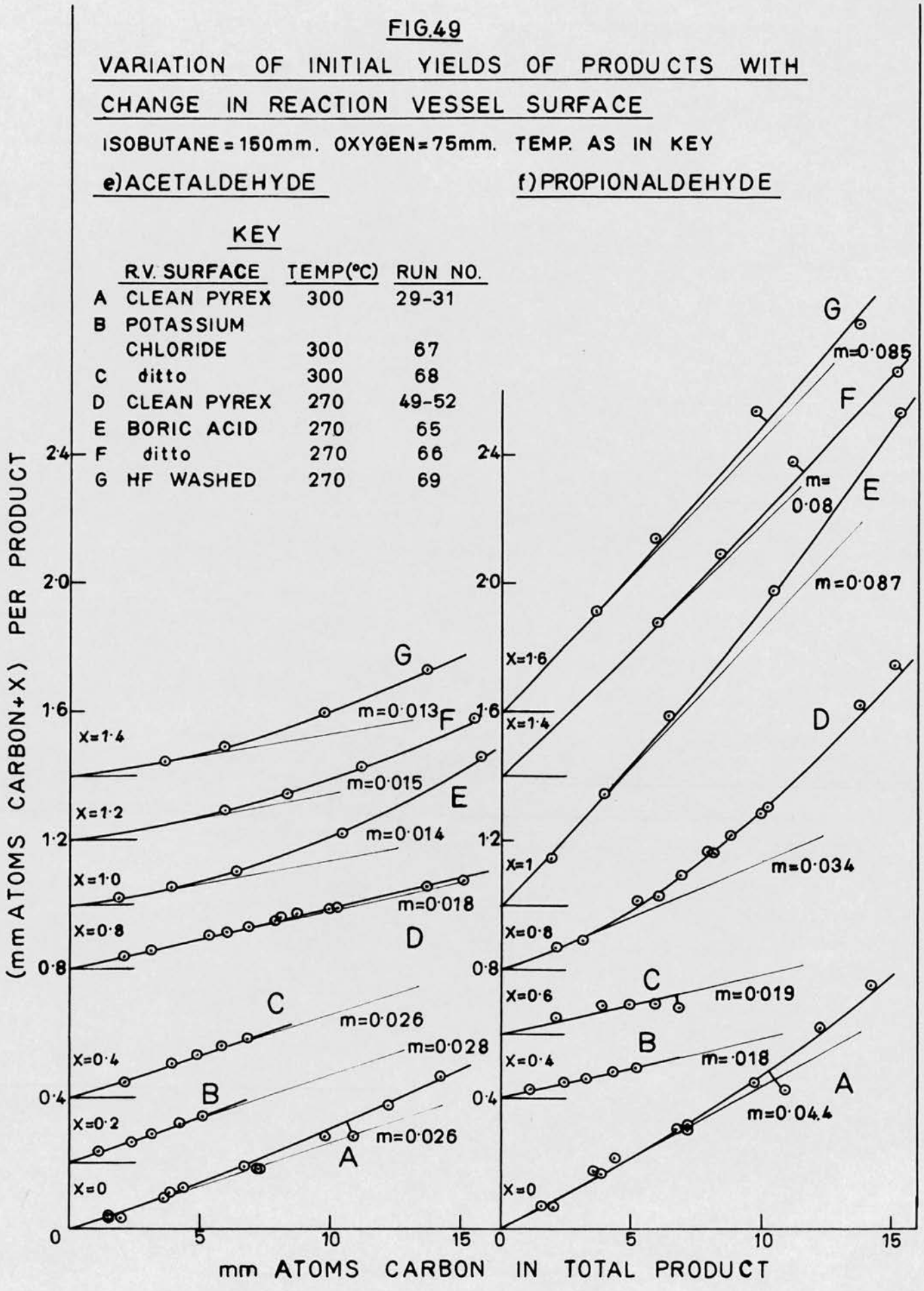


FIG.50

VARIATION OF INITIAL YIELDS OF PRODUCTS WITH CHANGE IN REACTION VESSEL SURFACE

ISOBUTANE = 150mm. OXYGEN = 75mm. TEMP. AS IN KEY

g) ISOBUTYRALDEHYDE

h) METHACROLEIN

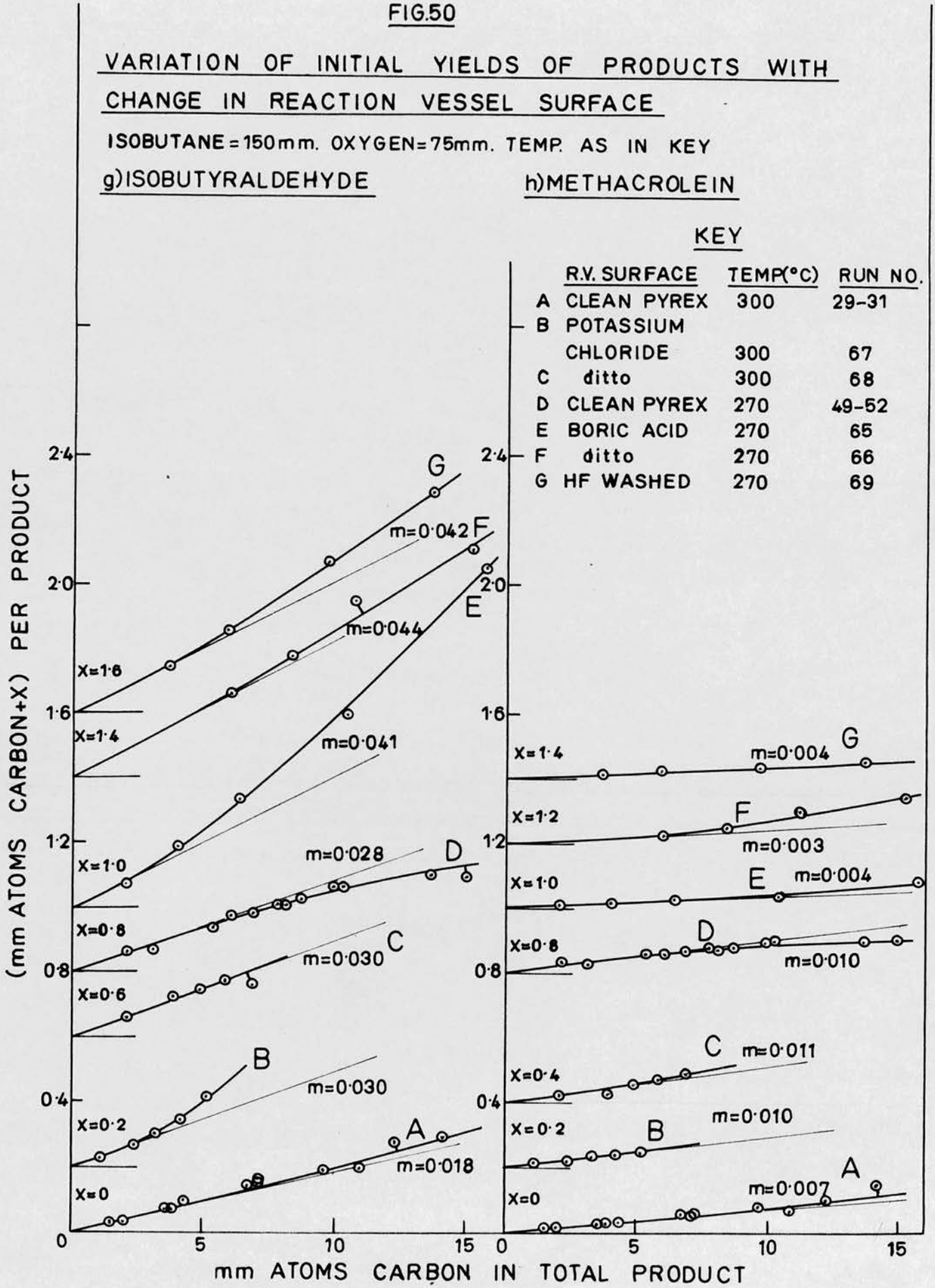


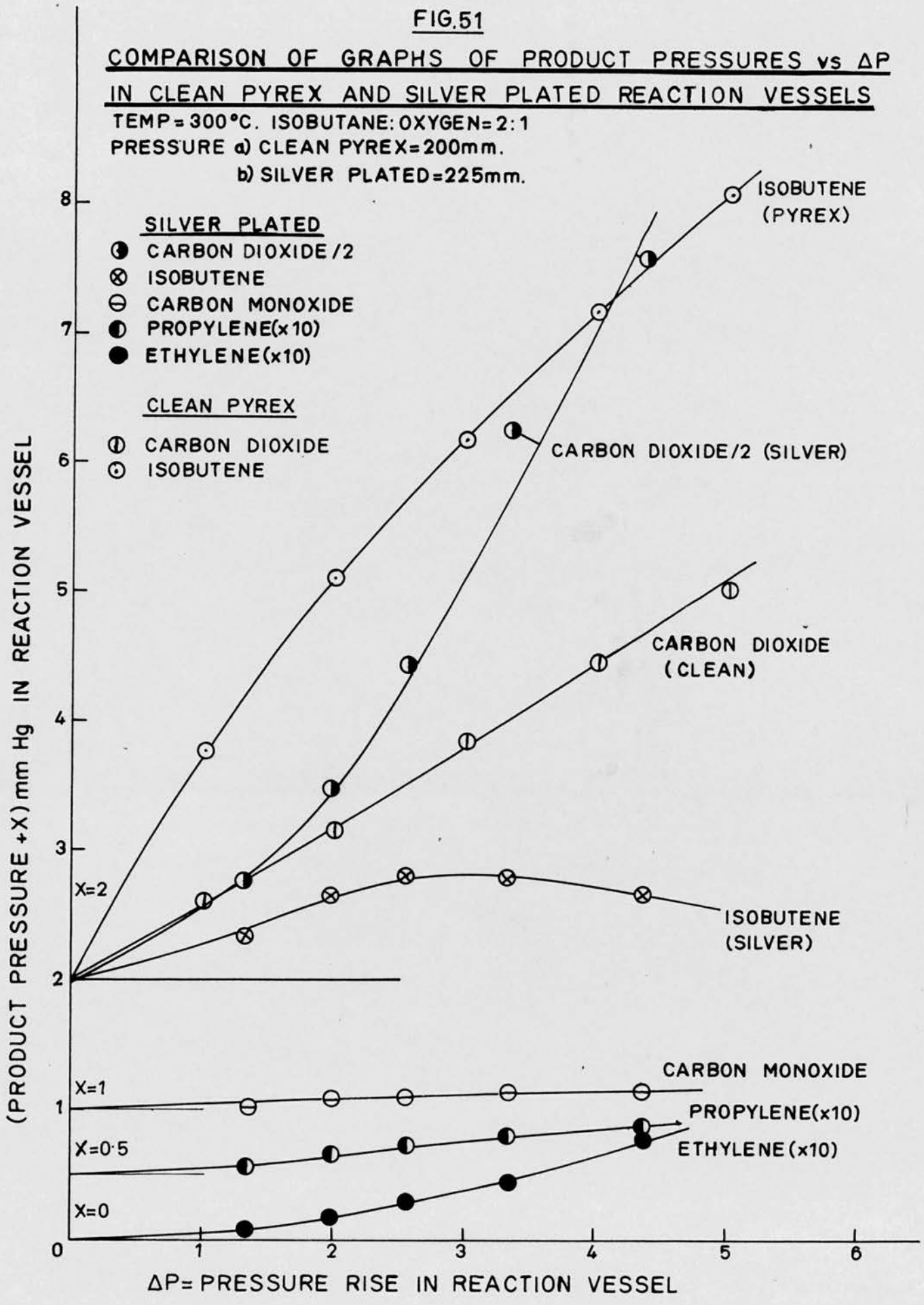
FIG.51

COMPARISON OF GRAPHS OF PRODUCT PRESSURES vs ΔP IN CLEAN PYREX AND SILVER PLATED REACTION VESSELS

TEMP = 300°C. ISOBUTANE: OXYGEN = 2:1

PRESSURE a) CLEAN PYREX = 200mm.

b) SILVER PLATED = 225mm.



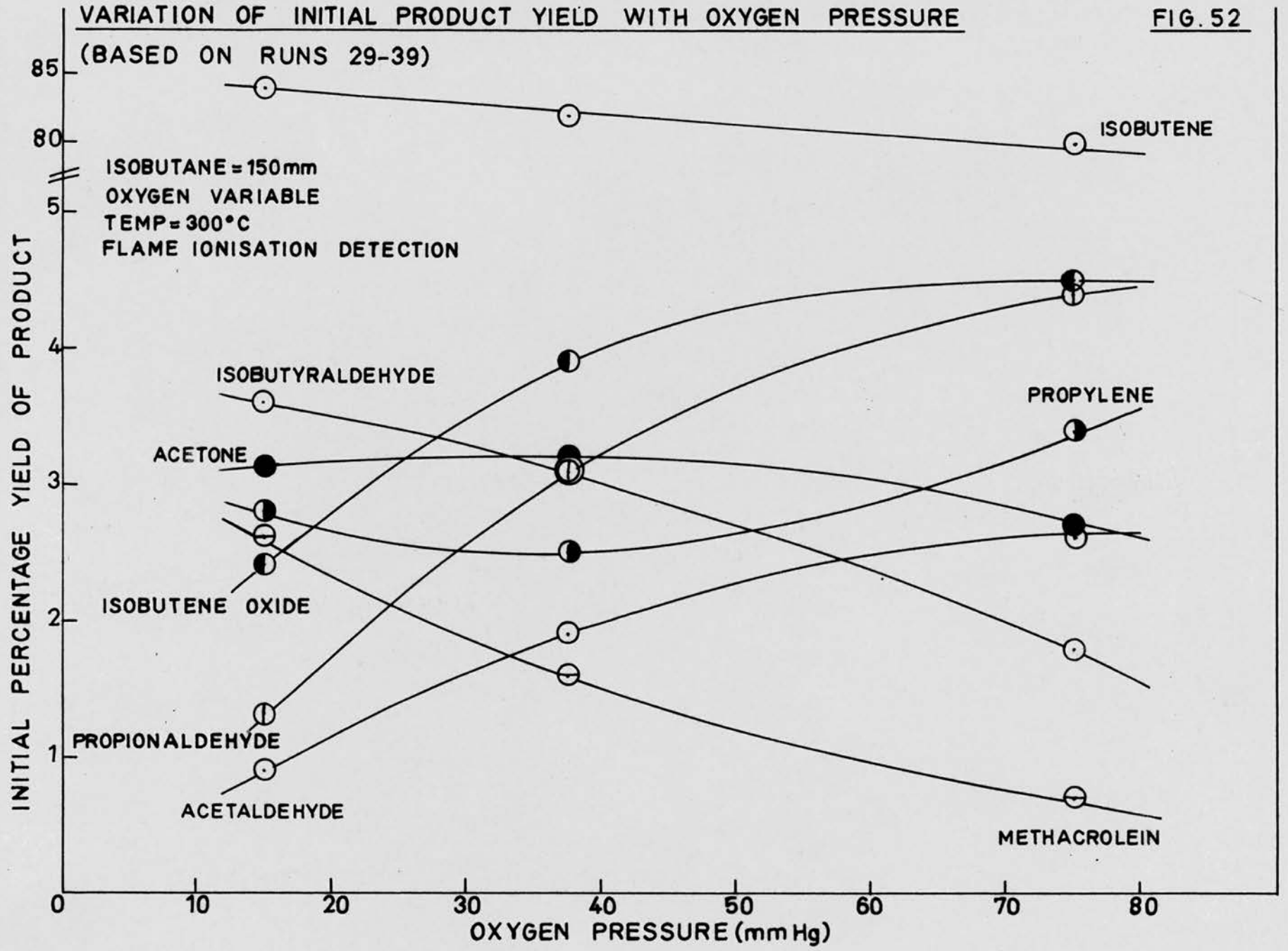

VARIATION OF INITIAL PRODUCT YIELD WITH OXYGEN PRESSURE
FIG. 52
(BASED ON RUNS 29-39)
ISOBUTANE = 150mm
OXYGEN VARIABLE
TEMP = 300°C
FLAME IONISATION DETECTION
ISOBUTENE
ISOBUTYRALDEHYDE
ACETONE
PROPYLENE
ISOBUTENE OXIDE
PROPIONALDEHYDE
ACETALDEHYDE
METHACROLEIN
INITIAL PERCENTAGE YIELD OF PRODUCT
OXYGEN PRESSURE (mm Hg)
85
80
5
4
3
2
1
0
10
20
30
40
50
60
70
80

FIG.53

VARIATION OF INITIAL PRODUCT YIELD WITH TEMPERATURE